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Photovoltaic Energy Systems Environmental Concerns and Control Technology Needs

Brookhaven National Lab.
Upton, NY

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PHOTOVOLTAIC ENERGY SYSTEMS: ENVIRONMENTAL CONCERNS AND CONTROL TECHNOLOGY NEEDS

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollution impacts on our environment and even on our health can require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory - Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

This report updates previous efforts to examine potential health and environmental risks and control technology needs related to photovoltaic energy systems. Waste streams and control technology requirements for three photovoltaic fabrication alternatives representing a range of manufacturing options and materials likely to be used were examined. This analysis should provide background information about potential health and environmental effects of photovoltaic energy systems to administrators determining research and regulatory priorities, and Federal, state, and county officials engaged in pollution control permitting programs. Further information on this subject can be obtained from the Energy Pollution Control Division of IERL-Ci.

David G. Stephan
Director
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ABSTRACT

Technical and commercial readiness for alternate photovoltaic energy systems, and waste streams from three different photovoltaic systems are examined. At present, specific emission standards for this industry do not exist and measurements of wastes produced by existing manufacturers are not available. Thus, emission estimates presented are based upon design engineering studies of expected typical facilities. Because of the widespread use of many of the materials used in this industry, available control experience and technologies used in other industries may ultimately be applied to photovoltaic plants. This analysis suggests that some uncontrolled waste streams could be declared toxic or hazardous under various provisions of the Clean Air, Clean Water, and Resource and Conservation Recovery Acts. Although some processes could emit large quantities of pollutants, these can be controlled using available technology. Other processes may emit small quantities of more toxic pollutants which will probably not be directly controlled unless significant health hazards are identified. Environmental problems in installation and operation are probably associated with large central-station applications; no significant effects are expected from small decentralized applications. Decommissioning of broken or degraded photovoltaic systems will generate large quantities of solid waste which can be simply disposed of in a landfill or perhaps recycled. Disposal of spent photovoltaic devices containing cadmium may present unique hazards.

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SECTION 1

INTRODUCTION

Identification and analysis of environmental concerns and ways to mitigate them for any energy industry, before it becomes fully commercialized, can limit potential investment costs while simultaneously minimizing environmental and public health risks. This type of analysis can also provide background information about potential health and environmental effects to planners determining research and regulatory priorities, and to Federal, state, and county officials engaged in pollution control permitting programs.

In this spirit, this study reviewed the technological readiness and examined environmental concerns related to commercialization of photovoltaic energy systems. This report: (i) describes the technical and commercial readiness of photovoltaic energy systems; (ii) reviews refining, fabrication, installation, operation and maintenance, and decommissioning alternatives associated with the industry; (iii) identified methods which are likely to be used to reduce pollutant release; (iv) describes environmental regulations that are, or might be, applied to an installed industry; and (v) examines the hazard potential of wastes generated during the refining of specific materials and the fabrication of different photovoltaic cell types. The information presented is based upon an extensive analysis of the literature, supplemented by discussions with different individuals in the governmental and private sectors.

This report principally considers the refining of materials used in producing photovoltaic cells and the subsequent fabrication of photovoltaic devices. These steps were intensively examined because they are specific to the photovoltaics energy cycle and account for the release of most of the pollutants under consideration. The waste streams and pollution control methods for three different photovoltaic systems were examined: (i) silicon n/p cells produced by ingot growing; (ii) silicon metal/insulator/semiconductor cells produced by ribbon growing; (iii) cadmium sulfide/copper sulfide backwall cells produced by spray deposition. These alternatives cover a range of manufacturing options and materials likely to be used in near-term commercialization activities. Installation, operation and maintenance and decommissioning of photovoltaic systems are briefly discussed at the end of the report. The environmental impacts which occur during these parts of a system's life cycle are summarized.

The information presented in this report is based upon an extensive analysis of the literature, supplemented by discussions with different individuals in the governmental and private sectors. Although measurements of waste streams from existing manufacturers of photovoltaic devices are not publicly available, design engineering studies of expected typical facilities for refining and fabricating the devices have been prepared.

SECTION 2

CONCLUSIONS

Current Industry and Future Growth

The U.S. photovoltaic industry is presently small, with production in the late 1970's of approximately 1 MWp per year. However large growth is expected in the next decade as this energy conversion technology becomes competitive in several new markets. Currently, small-remote (<10kWp) units are used in non-grid-connected applications. Use in this area is expected to increase. In addition, small (10 kWp) to large (100 MWp) systems are being examined to supply power to residences, commercial and institutional facilities and for use in central-station electricity generation.

There are also a variety of materials and cell concepts being considered for use in photovoltaic systems. Single-crystal silicon cells are currently produced commercially and serve as a standard of comparison for new materials and concepts. Production of these cells is costly and several alternatives are being investigated. Processes nearing commercial application include both ingot casting and ribbon growing for use in semicrystalline silicon solar cells.

Inexpensively produced thin films have the potential to yield photovoltaic cells at comparatively low production cost. A cadmium sulfide/copper sulfide photovoltaic cell manufacturer is about to begin commercial operation in the U.S. and amorphous silicon cells are being commercially produced in Japan. Polycrystalline gallium arsenide is also being considered for use in thin-film cells.

Sources of Pollutants and Pollution Control

Large-scale growth in this industry will be followed by the increased production of gaseous, liquid and solid wastes. The types and sources of pollutants resulting from manufacture of the three types of photovoltaic cells considered in this report are summarized in Table 1. Several processes could emit potentially large quantities of pollutants. Large quantities of fine particulate are discharged at electric arc furnaces which produced metallurgical-grade silicon (MG-Si). However, the silicon material demands of the photovoltaic industry are small compared to those of other industries and therefore this industry is not expected to contribute to significant growth in emissions of these particulates over the next decade. Further refinement of MG-Si by existing techniques consumes large quantities of hydrochloric acid, which must ultimately be disposed of. Etching of single-crystal silicon ingots generates spent acids, including hydrofluoric, which will require controlled disposal if the quantities are large.

Table 1
Summary of types and sources of pollutants

Media/Category	Pollutants	Fabrication Process: Si Ingot: Si Reduction	Si Purification	Ingot Growth	Cutting	Etching	Doping	Etching	Metallization	AR Coating	Si Ribbon: Ribbon Forming	Back Contact	Plasma Etch	Ion Implantation	Metallization	AR Coating	CdS: Electroplating	(CdI_2)	CdSex Preparation	CdS Application	Grid Formation	Ion Implantation	Metallization
1. Atmospheric:																							
1.1 Gas - Combustible	Cl, H, Chlorosilanes	•	•	•																			
1.2 Gas + Other	$SiCl_3$, $PSCl_3$, PH_3, Acids, Solvents, (HCN), * F					•	•	•	•	•		•	•	•	•	•			•	•	•		
1.3 Dust	Metals, Si, Cd	•	•	•	•							•			•	•			•	•			
2. Liquid																							
2.1 Acid	HF, HCl, HNO_3, H_2SO_4					•		•															
2.2 Metals	Cd, Cu, Au, Ni, Si																•				•		
2.3 Other	Chlorosilanes, Solvents, Slurry, Cutting Oils		•		•	•		•	•			•			•	•	•		•		•		
3. Solid																							
3.1 Hazardous	Cd, F + other compounds	•													•	•	•		•	•	•		•
3.2 Nonhazardous	Si compounds	•		•	•						•								•				

*HCN may be a byproduct of CdS cell production.

Silicon ribbon production, as anticipated, is a much cleaner production process than is the use of single-crystal silicon ingots. Nevertheless, small quantities of solvents and silver-based inks may require careful control.

Cadmium sulfide photovoltaic cell production is characterized by the use and release of cadmium and the production of large quantities of spent plating solutions containing various metals. Over the next decade cadmium emissions from the photovoltaic industry should be small relative to other sources of this pollutant. However, any large quantities of plating solution will have to be treated as hazardous wastes and will require controlled disposal.

Because the photovoltaics industry uses many materials which are widely used in other industries, available control experience and technologies may ultimately be applied to the photovoltaics industry. The final degrees of control is likely to be more precisely defined by specific design engineering studies seeking compliance with specific standards. Table 2 summarizes controls likely to be used in this industry.

Table 2
Review of control technology alternatives

Media/Category	Pollutants	Control Technology	Comments
1. Atmospheric			
1.1 Gas - Combustible	CO, H, Chlorosilanes	CO combustion, air dilution, chlorosilanes combustion to form muriatic acid	Tech. commonly employed, limits must be identified
1.2 Gas - Other	BCl_3, $POCl_3$, PH_3, Acids, Solvents, (HCN),* F	Air dilution, treat in lime scrubber and discharge liquor to lagoon	Design studies required to achieve limits
1.3 Dust	Metals, Si, Cd,	Bag filters or cyclones	97 - 99% Removal
2. Liquid			
2.1 Acid	HF, HCl, Acetic, HNO_3, H_2SO_4	Neutralization	Impervious lagoon, overflow liquid may be hazardous, sludge will be hazardous
2.2 Metals	Cd, Cu, As, Ni, Si	Flocculation (lime, alum, ferric salts, polyelectrolytes)	Flocculation technique must be identified. Effective standards must be met and sludge will require control
2.3 Other	Chlorosilanes, solvents, slurry, cutting oils	Process revisions, distillation	Chlorosilanes could be feedstock
3. Solid			
3.1 Hazardous	Cd, F + other compounds	Three alternatives - resale, recycle, disposal in controlled landfill	Metals + F noted under RCRA guidelines
3.2 Nonhazardous	Si compounds	Resale or disposal in municipal landfill	

*HCN may be a byproduct of CdS cell production.

Some photovoltaic manufacturing processes will emit small quantities of exotic pollutants (e.g. boron trichloride, phosphorous oxychloride, phosphine) for which no emission standards exist. It is not expected that they will be directly controlled unless significant health hazards are identified. However, to the degree that processes are integrated within this industry, a combination of waste recycling and control of major pollutant streams may also reduce discharges of these more exotic pollutants.

Studies to date indicate that the most significant environmental problems in operation of photovoltaic devices are probably associated with large central-station applications; no significant effects are expected from decentralized applications. It has been speculated that large facilities may produce micro- or meso-scale changes in the physical environment. Subsequent effects on species diversity, standing biomass, wind, temperature, and humidity have been hypothesized. Environmental impacts may also occur from the use of herbicides and panel cleaning solutions.

Decommissioning of broken or degraded photovoltaic systems will generate large quantities of solid waste. Most of these wastes will be recycled or landfilled. Disposal of large quantities of spent photovoltaic devices containing cadmium will probably require disposal in controlled landfills. Decentralized disposal by individual homeowners could result in the release of small quantities of cadmium to the atmosphere (from combustion at municipal incinerators) or to terrestrial and aquatic systems (from disposal in municipal landfills).

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Applicable Regulations

At the present time, specific emission standards for this industry do not exist, and regulations on existing facilities range from none to specification of methods of disposal of hazardous wastes. Because of process similarities, standards developed for related industries, processes or specific pollutants, may affect control technology requirements in this industry. Potential requirements under review by the Environmental Protection Agency include Clean Air Act National Emission Standards for Hazardous Air Pollutants for arsenic and possibly cadmium, and New Source Performance Standards for particulates from electric arc furnaces and volatile organic compounds from degreasing operations; Clean Water Act effluent standards for the electronics industry; and electroplating and degreasing operations, and a variety of specific pollutants.

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SECTION 3

RECOMMENDATIONS

On the basis of this analysis, the following topics may require further investigation:

(i) Measurement of Existing Waste Streams - Analyses of risks from photovoltaic energy systems are based upon design engineering estimates of wastes emitted from typical facilities. Sampling and chemical analyses from existing facilities are required to support the findings of these engineering studies or to identify inadequacies.

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(ii) Regulation of Existing Industry - At the present time, efforts to control wastes from the existing industry vary. Some state and county officials engaged in the regulation of the existing industry appear to need information concerning problems likely to be encountered and controls which could be employed. A large number of regulations exist, or are being developed, for related industries, processes, and/or pollutants. Potential applicability of these regulations to this industry needs to be examined in greater detail.

(iii) Technology Transfer - Manufacture of photovoltaic devices may require use and disposal of large numbers of chemicals; some may be toxic or hazardous. Control experience obtained for these materials in related industries should be made available to manufacturers of photovoltaic systems before facilities are actually constructed. Design engineering studies and field application of control techniques may ultimately be required to demonstrate their cost-effective applicability to the industry.

(iv) Evaluation of New Processes - Alternative materials and fabrication processes are being rapidly developed. Environmental data, however, are not being assembled at the same rate. Thus, existing knowledge about processing techniques, materials, and potential control methods is limited. Ongoing efforts are required to eliminate this void. Identification of control needs, prior to full-scale commercialization of these new technologies, can reduce total design engineering cost while minimizing potential health and environmental risks.

(v) Micro- and Meso-scale Biological and Climatic Effects - A number of analysts have suggested that operation of large central-station photovoltaic plants in the Southwest may create micro- and meso-scale effects on biological communities and climate. Research and analysis are required to evaluate the magnitude of these effects.

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SECTION 4

BACKGROUND

DEFINITIONS

Photovoltaic systems refer to a set of solar energy conversion technologies that convert light energy (photons) directly into electricity. This phenomenon, known as the photovoltaic effect, begins with the excitation of electrons in a solid by the absorption of light. This excitation creates a population of both negative and positive charges which are free to move through a semiconductor material when it contains appreciable numbers of impurity centers. When a semiconductor is specially treated (doped) with these impurities, it is capable of converting incident sunlight into electrical energy.

These specially treated semiconductor materials are called photovoltaic cells or solar cells. In order to produce useful energy, individual cells must be wired in series to increase the voltage and in parallel to increase the current. Groups of cells are connected to form modules, and groups of modules to form arrays. Modules and arrays must be held in place at the point of installation by support structures. Circuitry to control and modify electrical output is also needed. Energy storage (e.g., batteries) may be added to the system to provide energy during periods of reduced output. The combination of the arrays, support structures, controls, and storage are often referred to as a photovoltaic system. The photovoltaic energy cycle may include all steps from the extraction, preparation, and refining of raw materials, to the fabrication, installation, operation and maintenance, and decommissioning of the photovoltaic systems.

HISTORICAL OVERVIEW[1-4]

Although the photovoltaic effect was first observed in 1839, the first silicon solar cell of reasonable efficiency was not developed until 1954. This, interestingly, corresponded with the development of a process to purify silicon monocrystals. Spinoffs from this process included not only development of the silicon solar cell, but also transistor technology.

A first assessment of conversion efficiencies attainable for all semiconductor materials was published in 1956. At that time, most interest was centered on monocrystal or single-crystal silicon alternatives, but the photovoltaic effect was also being examined in other materials - cadmium sulfide, gallium arsenide, and cadmium telluride. At present, a large variety of materials and cell concepts are being examined. Those showing

greatest promise include silicon technologies, thin films, and concentrators.

Single-crystal silicon cells are currently produced commercially and serve as the standard of comparison for new materials and concepts being developed. Production of these cell types is, however, costly and several silicon alternatives are being investigated. Processes nearing commercial application include both ingot casting and ribbon growing.

Inexpensively produced thin films represent an alternative to existing fabrication technologies. Thin-film cells include a large group of materials processed in a similar way. Thin films of specialized materials such as cadmium sulfide/copper sulfide, polycrystalline gallium arsenide, and amorphous silicon have the potential to yield photovoltaic cells at comparatively low production costs. The major disadvantages of thin films are their low efficiencies and short lifetimes.

Existing photovoltaic technologies are expensive because of the diffuse nature of sunlight. Concentrators offer one alternative to overcome this problem, but use of concentrators, instead of flat-plate collectors, increases engineering complexity (e.g., additional support and cooling will be required) and capital costs of the photovoltaic systems. Many analysts have concluded that cell efficiencies of ~30% (~2 times greater than that of single-crystal silicon ingot cells) are required for concentrators to be cost effective.[2]

PAST, PRESENT, AND FUTURE MARKETS[1]

After the development of the silicon cell in 1954, commercial efforts were initiated. Early sales in 1955-1959 of single-crystal silicon cells were for terrestrial applications. Following the launch of the first satellite in 1958, silicon cells became the principal power source for all satellites, and most sales were made for this application. Photovoltaic cells subsequently enjoyed great commercial success in this market because they were found to be lighter than any other power source when weight of fuel and potential energy output were considered.

In 1975, the world production rate of silicon solar cells for use in space was about 100 kWp/year, a rate that had remained constant for about 15 years. In 1975, for the first time, more solar cells were sold for use on the ground than in space. In view of the fact that the terrestrial market was insignificant in 1973, this represented a tremendous growth in demand.[4] In 1976, the free-world market for photovoltaic cells was about 308 kWp, of which ~208 kWp were sold by U.S. manufacturers. The U.S. government at that time bought ~108 kWp, of which ~50 kWp were used in satellites. Major commercial sales also included communications equipment (~68 kWp), corrosion protection for bridges, pipelines, and similar applications (~28 kWp), and aids to navigation (~20 kWp).[5] Sales during 1977 were about twice those of 1976. Sales for 1978 have been estimated to be over 1 MWp with shipments on the order of 700 to 800 kWp. No estimates for 1979 sales are available, but preliminary discussions with industry representatives indicate that sales

may have again exceeded 1 MWp. Approximately half of these current sales are to foreign markets.[2]

Future growth in this industry is expected to be quite large. The most widely held view of photovoltaic development is that the technology will penetrate stepwise three different markets. The near-term market generally includes small remote-sited applications, e.g., mountaintop radio-repeaters. Commercial sales are currently being made in this market; annual sales of 3 to 7 MWp are expected. An intermediate market, e.g., water pumping and general power supplies for remote villages, could ultimately range from 50 to 500 MWp annually. Photovoltaic systems are not yet cost competitive for this market. The ultimate market for photovoltaic energy systems will be the large electric power-using sectors, comprising small (<3 to 10 kWp), intermediate (<500 kWp), and large (~100 MWp) installations serving single residences, commercial and industrial settings, and central-station generators, respectively. The potential size of this last market varies according to the projected costs of photovoltaic and conventionally generated electricity.[2]

In Table 3, estimates of the potential role to be played by photovoltaic energy systems in the U.S. energy economy are given. In order to meet these goals, massive growth in the industry is required. In Figure 1, we plot projected annual energy demand and cumulative installed capacity required to meet the Department of Energy minimum (0.1×10^{18} J) and maximum (1.1×10^{18} J) goals identified in Table 3. As noted, even in the low case, an annual growth rate of 63% per year would be required. In the high case a growth rate of 83% per year is required. The accuracy of these estimates and the ability of the industry to grow at this rate have been questioned. For comparison, the value of shipments from the semiconductor industry only increased by a factor of ~10 over a seventeen year period extending from 1960 to 1977. Reductions in Federal research and development funds for photovoltaic research may increase the difficulty of meeting these goals.

Table 3
Photovoltaic energy supply projections

Reference	Year	Projected Supply (10^{18} J)
Council on Environmental Quality[6]	2000	2.1 - 8.4
Council on Environmental Quality[6]	2020	11 - 32
Office of the President[7]	2000	0.11 - 1.1
Department of Energy[8]	2000	0.11 - 1.1
Audubon Society[9]	2000	0.74

MATERIAL AND MANUFACTURING OPTIONS

In 1979, at least 8 U.S. companies were producing terrestrial photovoltaic modules in commercial quantities. All of the companies produced single-crystal silicon flat-plate modules. Prototypes of polycrystalline and concentrating modules, using single-crystal silicon,

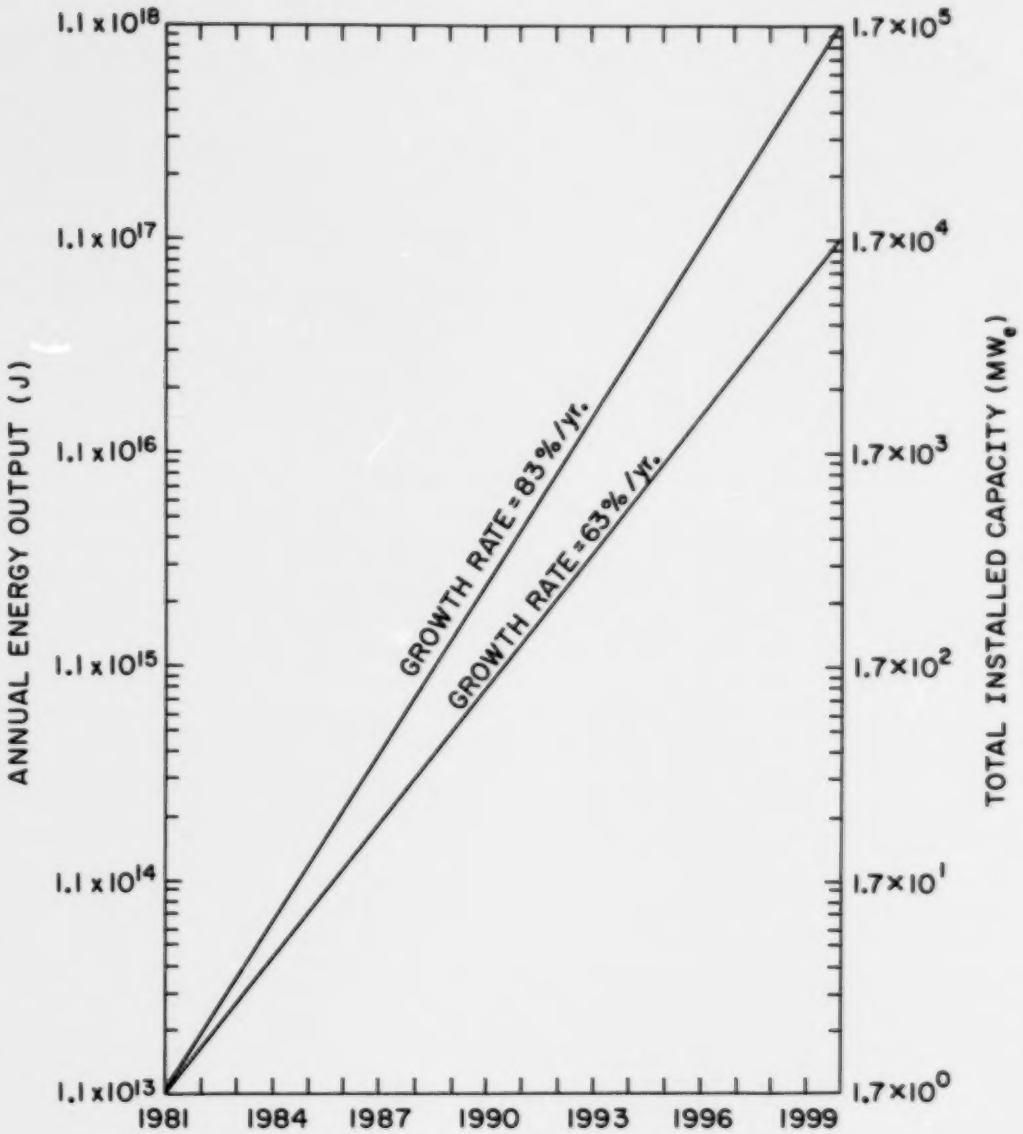

Figure 1. Projected growth in the photovoltaics industry.

have been successfully produced[1] and commercial sales are imminent. Similarly commercial production of cadmium sulfide/copper sulfide modules is about to begin. At least 10 additional U.S. companies are investing significant amounts of private capital in photovoltaics research and development to supplement the funding provided by the U.S. Department of Energy (FY 1981 = $1.5 x 10^8; FY 1982 ~$7.4 x 10^7). Plans for commercial production of single-crystal, and concentrating gallium arsenide modules are now being formulated. Other technologies, such as thin-film silicon, gallium arsenide, and indium phosphorous, polycrystalline gallium arsenide, and advanced concentrator materials will require substantial research before commercial production can begin.[1-4]

INDUSTRY STRUCTURE

Manufacturers of photovoltaic devices (Table 4) may be divided into three different classes. In the first category are a few small businesses which produce photovoltaic modules or systems as their primary product line (e.g., Solenergy). In these companies, current sales and service are important to their continued flexibility. In the second category are companies associated with moderate or large electronics firms (e.g., Texas Instruments, RCA, Motorola), which view photovoltaics fabrication as another semiconductor product line. The third group is composed of companies affiliated with major international energy companies (e.g., Exxon, Mobil, Shell, Atlantic-Richfield), which are characterized by their desire to diversify into non-oil energy sources and the availability of capital to support new ventures.[1] Estimates of market shares for each of these groups are not available.

Table 4
Commercial flat-plate photovoltaic module manufacturers - April 1981[10]

Applied Solar Energy Corp.	Silicon Sensors, Inc.
Arco Solar Inc.	Solar Power Corp.
Free Energy Systems, Inc.	Solarex Corp.
Mobil Tyco Solar Energy Corp.	Solec International, Inc.
Motorola Inc.	Solenergy Corp.
Photon Power, Inc.	Sollos, Inc.
Photonwatt International, Inc.	Tideland Signal Corp.
SES, Inc.	United Energy Corp.

EXISTING ENVIRONMENTAL ANALYSES

Potential health and environmental effects of photovoltaic energy systems are documented in at least 20 different studies.[11-33] Detailed review of each of these studies is beyond the needs of this presentation. Instead, overall concerns are summarized for three different areas: public health, occupational health, and environmental quality.

Public Health

Although it commonly argued that photovoltaic energy systems operate noiselessly and without pollution, a fallacy exists. Indeed, photovoltaic systems, in contrast to many other energy alternatives, do not produce combustion by-products during operation. However, pollutants are generated by material production and device fabrication activities, and these must be examined in order to estimate potential public health risks associated with this energy system.

Materials required for photovoltaic fabrication include many common substances used throughout industry (e.g., aluminum, iron and steel, concrete, copper, etc.) and others whose use is somewhat limited (e.g., cadmium and silicon). No new environmental or public health risks are expected from the production of commonly used materials, but rather a reapportionment of the risk which already exists.[33] These risks relate to release of pollutants (e.g., SO_x, NO_x, CO_2, etc.) both to the atmosphere and to aquatic systems. Some of these pollutants (e.g., SO_x) are thought to endanger public health. For this reason, estimates of the quantities of SO_x emitted under different fabrication alternatives and scenarios are presented in many of the available reports. These are summarized in Table 5.

Table 5
Estimates of SO_x releases from the photovoltaic energy cycle*
($MT/10^{15}$ J)

Reference	Estimate
Inhaber[20]	†
Mintzer et al.[19]	2.4 - 99
Department of Energy[30]	†
Moskowitz et al.[27]	25 - 120
Moskowitz et al.[33]	12 - 1100

*A coal-fired power plant meeting 1979 new source performance standards and burning 2% sulfur bituminous coal would emit 260 $MT/10^{15}$J SO_x.
†Calculated but not directly available from the published reports.

Production of the less commonly used materials, may present new or greater risks than now experienced. Specifically, production of metallurgical-grade silicon creates large quantities of fine particulates, and production of solar-grade silicon using a conventional refining process (i.e., Siemens) is known to be highly inefficient. Because of these recognized problems, new silicon processing alternatives are being developed (e.g., Union Carbide). Production and use of cadmium and arsenic have also aroused considerable concern because of the toxic and carcinogenic properties of these materials.

At photovoltaic fabrication facilities, a large number of toxic and hazardous materials are used in the crystal growing, etching, and doping processes. Some of these materials will ultimately be released to the environment in the liquid, solid, or gaseous waste streams from fabrication plants. Because actual measurements of types and quantities of these materials emitted are generally not available, estimates are usually based

upon design engineering studies. Updated design engineering studies for new fabrication alternatives are needed.

Finally, disposal of spent photovoltaic devices containing arsenic and cadmium has also aroused concern. Although the quantities of the specific materials present in each photocell are quite small, the total mass present in the large number of devices to be fabricated may, in fact, be quite large. Upon disposal, some of these materials (e.g., cadmium) may leach from broken photovoltaic systems and transfer through the food chain.

Occupational Health

The development of any energy system requires labor to extract and process materials, and to fabricate, install, operate and maintain, and decommission devices used to convert alternative forms of energy into more usable states. This resultant labor demand is distributed among many occupational activities. Each occupation inherently possesses different physical and chemical working environments which can affect worker health and safety.

Both the type and size of the labor force required,and the types of risks likely to be confronted, are analyzed in detail in a small number of reports.[22,24,26] As with other questions relating to public health, problems associated with the types and quantities of toxic materials used in this industry have aroused considerable concern. It should be noted that the National Institute of Occupational Health and Safety (NIOSH) and the Environmental Protection Agency (EPA) - Cincinnati, are jointly sponsoring a study to define controls to be employed in the semiconductor industry and safe levels of occupational exposure to various compounds.

Environmental Quality

Effects on environment can be expected from chemicals released throughout the photovoltaics energy cycle and from physical disturbances caused by construction and operation of central-station photovoltaic facilities. Decentralized or rooftop photovoltaic facilities are not expected to disrupt the physical environment to any great extent.

No significant or new disruptions are anticipated from the extraction of the conventional materials used throughout industry, nor are problems with respect to silicon extraction; note that cadmium and arsenic are by-products of the production of other metals (e.g., copper and zinc) and are not directly mined. Transportation of some materials (e.g., acids, caustics, and other toxic substances) used in photovoltaic cell fabrication, however, raises the prospect of inevitable spills of tank car volumes and chronic low-level releases of those materials. Such release could lead to acute local ecological disruption or contribute to chronic regional pollution problems. Environmental mobilities of some materials related to potential photovoltaic fabrication facilities (i.e., arsenic, boron, cadmium, copper, fluorine, gallium, indium, nickel, palladium, selenium, silicon, and tellurium) may be hazardous to biota. Of these trace elements, arsenic, selenium, and cadmium have aroused the greatest concern since

natural mechanisms for concentrating these materials to toxic levels in terrestrial food webs have been observed.

Potential for environmental disruption may also relate to the installation of large central-station facilities. Deployment of a 1000-MWp central-station plant would require approximately 30 km^2 of photovoltaic panel and perhaps twice that in land area when access roads and service buidings are taken into account. These plants might be located in the arid regions of the Southwest because of high insolation and land availability.

Aside from the obvious and direct disruption of the land during site preparation and plant operation, other indirect effects that could be expected include changes in the micro-climate by shading the surface from the incoming solar radiation, altering soil temperature and soil moisture, and modifying wind flow patterns. Subsequent changes in both species diversity and standing biomass are a possibility.

It has also been speculated that meso-scale climatic effects may occur. Physical factors likely to be affected include changes in surface albedo, roughness, porosity, emissivity, thermal conductance, heat capacity, and the remission ratio. Changes in these characteristics could create variations in wind, temperature, and humidity.

SECTION 5

APPLICABLE ENVIRONMENTAL LEGISLATION

BACKGROUND

Federal regulations specific to the photovoltaics manufacturing industry have not yet been published. Some facilities now in operation are regulated as parts of other industries. Many existing regulations for industries such as electroplating, glass manufacture, and inorganic chemicals production could apply to processes used in photovoltaics manufacture (Table 6). Substantial growth in this industry could prompt the development of specific regulations.

Table 6
Industries related to photovoltaic cell fabrication specifically addressed by Federal environmental regulations[31]

	Regulatory Programs					
	Clean Air Act		Clean Water Act			RCRA
	NESHAP	NSPS	Effluent Limits	Pretreatment Standards	Toxic Standards	Hazardous Waste
Electronic Component Production					X	X
Electroplating			X	X		X
Ferroalloy Manufacturing		X	X			X
Glass Manufacturing	X					
Ink Formulating	X					X
Chlorine Production						X
Sulfuric Acid Plants		X				
Iron and Steel Manufacturing		X	X			
Mineral Mining and Processing			X			
Nonferrous Metals Manufacturing		X	X	X		
Paint Formulation			X			X
Plastics And Synthetics Manufacturing			X			

Federal legislation of concern includes the Clean Air Act (CAA),[34] the Clean Water Act (CWA),[35] and the Resource Conservation and Recovery Act (RCRA).[36] The U.S. Environmental Protection Agency (EPA) has the statutory responsibility for administering and enforcing the regulatory programs

designed to carry out the provisions of the three acts. Responsibility for some of the programs has been delegated by EPA to the states which, in turn, have further delegated responsibilities to county authorities. In addition, state and county authorities may impose more stringent requirements than required by Federal law. In the absence of specific Federal guidelines, state and county authorities can establish their own standards. Provisions of the three Federal acts are discussed and current regulatory programs applied to the photovoltaics manufacturing industry described.

CLEAN AIR ACT (CAA)

CAA regulations provide for a number of enforcement programs.

New Source Performance Standards (NSPS)

NSPS apply to stationary sources constructed, or modified, after the publication of applicable standards. They have been specified for 26 major industrial source categories and are formulated to reflect the best available control technologies considering economics for each source.

Pursuant to the requirements of this act, EPA is also developing NSPS to control particulate emissions from electric arc furnaces at ferrous foundaries[37] and volatile organic compounds (VOC) from metal cleaning and degreasing operations.[38] The former may affect silicon refining operations, while it is expected that the latter will be applicable to cell fabrication facilities because proposed VOC regulations are process-specific.

National Emission Standards for Hazardous Air Pollutants (NESHAP)

NESHAP set limits on emissions of very hazardous air pollutants. At the present time, NESHAP are being developed for arsenic. These will not apply to any of the fabrication techniques reviewed, although large-scale commercialization of gallium arsenide devices may require closer examination. Also, determinations are currently being made for cadmium. Recent discussions with EPA officials, however, suggest that cadmium will not be declared a hazardous air pollutant.[39]

Prevention of Significant Deterioration (PSD) and Non-Attainment (NA)

PSD and NA reviews have been made for the 247 Air Quality Control Regions (AQCR) nationwide. They identify those AQCR, which are complying with National Ambient Air Quality Standards for criteria pollutants. Since photovoltaic fabrication facilities are not expected to be large generators of these conventional pollutants, these standards will not be directly invoked. Large-scale production of silicon, however, may conflict with these PSD requirements because of the potential release of large quantities of particulates and therefore need to be considered.

CLEAN WATER ACT (CWA)

The Clean Water Act sets two goals: (i) the achievement of fishable and swimmable waterways by 1983; and (ii) the achievement of zero discharge

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of pollutants by 1985. To reach these goals, a number of regulatory programs have been undertaken.

National Pollutant Discharge Elimination System (NPDES)

Under this program, states have the authority to issue permits for point source discharges. Applicants for permits must provide detailed information on effluent flow, composition, and treatment. Applicants within certain "primary" industries having production processes related to photovoltaic fabrication facilities are shown in Table 7. These industries must provide quantified data for a list of organic toxic pollutants, according to the fractions of volatile, acid, base/neutral, and pesticide. At present, permit applicants must apply best practical control technology (BPT). By mid-1984, dischargers of "conventional" pollutants must apply best conventional control technology (BCT), and dischargers of "nonconventional" must apply best available control technology (BAT).

Table 7
"Primary" industries required to obtain
National Pollutant Discharge Elimination System permits

Battery Manufacturing	Nonferrous Metals Manufacturing
Coil Coating	Ore Mining
Copper Forming	Paint and Ink Formulation
Electrical and Electronic Components	Photographic Equipment and Supplies
Electroplating	Plastics Processing
Foundries	Plastic and Synthetic Materials Manufacturing
Inorganic Chemicals Manufacturing	

Of particular interest are the ongoing activities to develop effluent guidelines for the "Piezoelectric Crystals, Semiconducing Crystals, Phosphorescent Coatings, and Magnetic Coating Segments of the Electrical and Electronic Product Point Source Category"[48] and the "Electrical and Electronic Components Category"[49] which includes the semiconductor industry. Because of similarities in the production processes, regulations established under these rule-making procedures could be applied to the photovoltaics industry.

Other CWA Programs

Waste streams discharged to municipal sewers must conform to pretreatment standards issued by EPA. In addition, EPA has published a list of "toxic" pollutants, for which effluent standards exist, and a list of "hazardous" pollutants, which may be regulated through NPDES permits, or on a case-by-case basis. Materials classified as toxic or hazardous and used by the photovoltaics industry during materials refining and fabrication are summarized in Table 8.

Table 8
Toxic and hazardous water pollutants

Arsenic and compounds	Lead and and compounds
Benzene	Nickel and compounds
Cadmium and compounds	Silver and compounds
Carbon tetrachloride	Thallium and compounds
Copper and compounds	Zinc and compounds
Cyanides	
Fluorides	

RESOURCE CONSERVATION AND RECOVERY ACT (RCRA)

RCRA provides guidelines for the protection of ground water, surface water, and ambient air from hazardous waste contamination. Nonhazardous waste disposal is seen by the EPA as a less severe problem, and is left primarily to state and local governments. Under RCRA, states are required to identify their responsibilities for hazardous waste management, and to encourage resource recovery and conservation. They must also apply and enforce environmentally sound disposal practices.

The Hazardous Waste Management (HWM) program will eventually provide "cradle-to-grave" management of hazardous wastes. Rules have not yet been fully implemented. Under the HWM program, EPA must identify the characteristics of hazardous wastes and establish special management requirements for them. Strict standards for specific materials have been set for proper record keeping, labeling, packaging, and transportation of hazardous wastes, as well as for facility siting, inspection, personnel training, emergency planning, etc.

Materials identified as toxic or hazardous under the RCRA guidelines and used in photovoltaic energy cycles are summarized in Table 9. In addition to these materials, EPA also identifies electroplating and degreasing operations as generators of hazardous waste.

Table 9
Toxic and hazardous wastes

Acids	Hydrofluoric Acid
Acetone	Lead and Compounds
Alcohols	Mercury and Compounds
Arsenic and Compounds	Nickel and Compounds
Benzene	Phosphine
Cadmium and compounds	Selenium and Compounds
Chlorosilanes	Silver and Compounds
Cyanides	Sulfides
Fluorine	

REGULATION OF EXISTING FACILITIES

In order to identify the types of regulations applied to existing photovoltaic cell fabrication facilities, a series of telephone interviews[40] were conducted with Federal, state, and county officials potentially engaged in the pollution control permitting programs of thirteen existing facilities (Table 10). From these discussions it was noted that although Federal and state regulations exist for many conventional air pollutants, photovoltaic plants are not large sources of these emissions. Seven of the thirteen facilities examined were unknown to the air pollution regulators in their areas. Two others were exempt from any required permits, and two more were in the process of applying for permits. The remaining two plants had several permits for individual pieces of equipment, such as scrubbers, ovens, and degreasers.

Table 10
Existing environmental control programs reviewed

Applied Solar Energy Corporation	Solar Power Corporation
ARCO Solar, Inc.	Solarex Corporation
Motorola, Inc.	Solec International, Inc.
Photon Power, Inc.	Solenergy Corporation
Photowatt International, Inc.	Sollos, Inc.
SES Inc.	Tideland Signal Corporation
Silicon Sensors, Inc.	

Liquid emissions are also unregulated at Federal and state levels: most facilities discharged their liquid wastes into the municipal sewer systems of the towns in which they were located. They must comply with municipal sewer ordinances for industrial users, and pretreatment programs are being developed by the EPA. A relatively common liquid waste problem reported was low pH. At least three of the facilities are required to neutralize liquid emissions. Five facilities are unknown to local water pollution regulators in their areas, possibly because of the small size or absence of a liquid waste system.

Large quantities of solid waste are not generated. Five facilities are, however, identified as hazardous waste generators. All are technically "small," according to RCRA standards i.e., less than 1000 kg per month. Identified wastes included: cyanide, acetone, other solvents, water-reactive materials, lithium, arsenic, and beryllium.

SECTION 6

SOURCES OF ENVIRONMENTAL RISK

The photovoltaic energy cycle includes the extraction, processing, and refining of raw materials and the fabrication, installation, operation and maintenance, and decommissioning of spent devices. In this analysis, considerable effort was spent examining potential environmental risks related to the refining of specific materials (e.g., silicon and cadmium) used in the active portion of different photovoltaic devices and their subsequent fabrication. These steps were intensively examined because they are specific to the photovoltaic energy cycle and represent major steps from which pollutants are released. Other areas also examined include installation, operation and maintenance, and decommissioning.

In refining, three alternatives were reviewed: (i) silicon refining by the Siemens process; (ii) silicon refining by the Union Carbide process; and (iii) cadmium and cadmium chloride production. The Siemens process is the technique currently employed to produce pure silicon used in the semiconductor industry. The Union Carbide process represents a newly proposed technique to reduce silicon production costs. For cadmium and cadmium chloride production, only one sequence was examined; no major alternatives are being explored.

In photovoltaic cell fabrication, three different alternatives were considered: (i) single-crystal silicon cells produced by ingot growing; (ii) semicrystalline silicon cells produced by a ribbon growing; (iii) thin-film cadmium sulfide/copper sulfide backwall cells produced by spray deposition. These alternatives cover a range of manufacturing options and materials likely to be used in near-term commercialization activities. Other processes nearing commercial viability include silicon cells produced by dendritic web, ingot casting and amorphous processes. Risks from these alternative processes may be different from those examined.

In the analysis, production processing requirements have been identified, material inputs and outputs quantified, availability of control technology reviewed, applicable environmental regulations noted, and hazard potential discussed. Emission estimates presented are based upon prudent engineering practices, especially with respect to toxic and hazardous pollutants. Since environmental hazards related to installation and to operation and maintenance are generally common to all photovoltaic systems, they are discussed without regard to the specific photovoltaic cell type. For the remaining steps, discussions are disaggregated by photovoltaic cell

type. Effects related to extraction of all materials and refining of materials commonly used throughout industry are not discussed.

The discussion in this report, and in the appendix, considers three categories of emissions: gas stream, liquid, and solid. Gas streams include any emission involving a gas or vapor, or exhaust gas streams carrying dusts. It is to be understood that these characterizations refer to the actual point of discharge from the process, since, in the course of treatment and disposal, these streams are likely to be converted from one medium to another. Pollutants in a gas stream, for example, might be removed by scrubbing with a liquid, and thus yield a liquid disposal problem. Another example would be the precipitation of heavy metals from a liquid emission, which would lead to a solid disposal problem.

Emission rates for the process steps examined are generally reported in units of (kg/day)/plant. For the refining processes, we assume that each refinery would produce 1000 metric tons per year of silicon or cadmium. All statistics for the fabrication facilities assume annual production capacities of 10 MWp. The 10-MWp plant is about equal to the projected size of a photovoltaic fabrication facility likely to be constructed in the late 1980's[41]: the largest production line in existence is ~1 MWp. Fabrication emission rates are also reported in units of (metric tons/year)/GWp. Annual production of 1 GWp, projected for around 1990 in the high case scenario and for 1995 in the low case scenario (Figure 2), would thus require 100 facilities each with a production output of 10 MWp.

The emission rates presented on a per plant basis provide background information for personnel engaged in pollution control permitting programs. In contrast, estimates presented on a per GWp basis should be more useful for decision-makers determining research and regulatory priorities. Caution should be exercised in using these data because they are not based upon measurements of waste streams from existing plants, but rather, upon extrapolations from pilot facilities and design engineering studies.

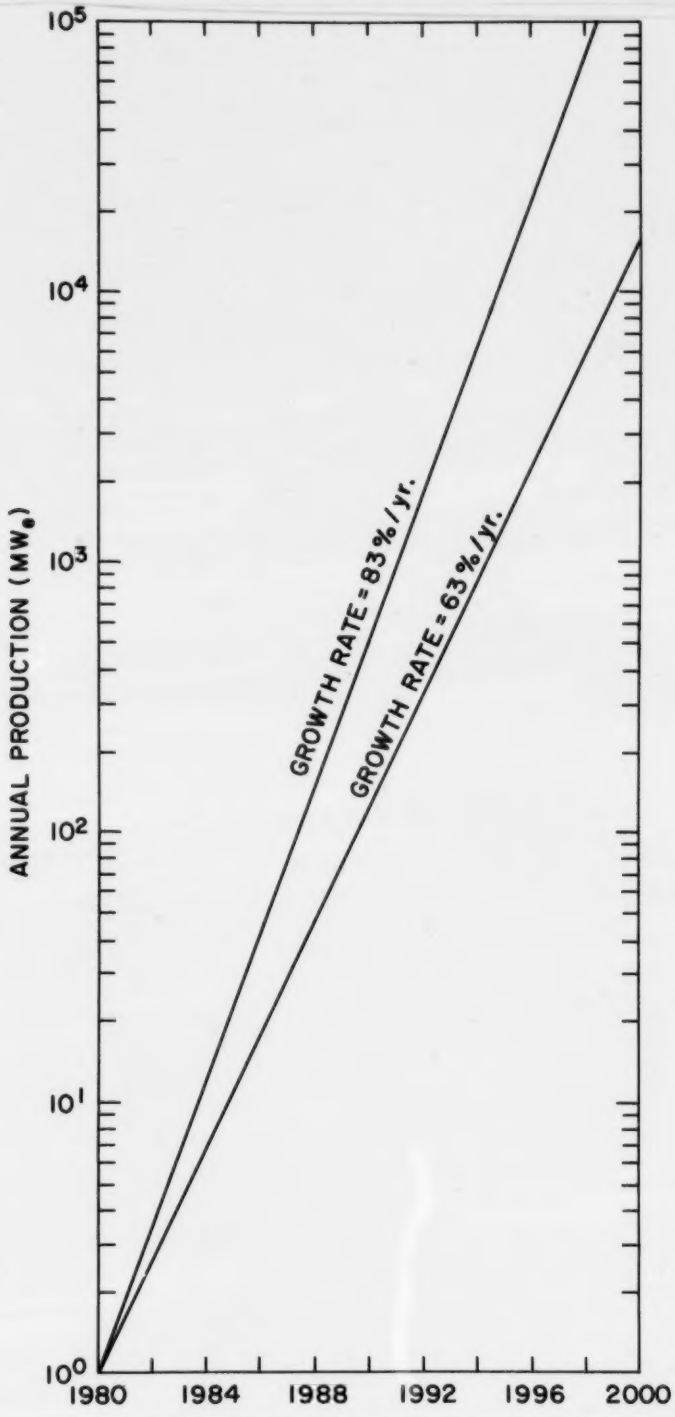

Figure 2. Estimated annual photovoltaic cell production rates.

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SECTION 7

PRODUCTION OF SINGLE-CRYSTAL SILICON CELLS

The refining and manufacturing steps required to produce a single-crystal silicon cell are shown in Figure 3. Note that either the Siemens process or the Union Carbide process can be used to produce semiconductor-silicon. In Table 11, emission estimates for these processes are summarized. Detailed documentation for these estimates are presented in Appendix A, where most of the references will be noted. Highlights are summarized below.

Also, presented below are brief descriptions of each processing step, followed by a discussion of the controls likely to be employed for the gaseous, liquid, and solid waste streams. These control estimates are based upon product design engineering practices; specific standards for this industry have not yet been promulgated.

PRODUCTION OF SEMICONDUCTOR-GRADE SILICON BY THE SIEMENS PROCESS

Process Description

The first step in this process is the production of metallurgical-grade silicon by the carbothermic reduction of silica. This requires the mixing of quartz with coke in an electric arc furnace which is heated to 1000°C. The carbon in the coke reduces the silica of the quartz to elemental silicon, forming carbon monoxide in the process. The silica contains impurities, as does the coke. The products include silicon containing 2 to 3% of the heavy metals, a gas consisting mostly of carbon monoxide and other impurities arising from volatile contaminants in the coke, and a dust-containing ash and silicon monoxide. The silicon product is called metallurgical-grade silicon (MG-Si). Finely ground MG-Si is reacted with hydrochloric acid forming a chlorosilane mixture. From this mixture, a stream of trichlorosilane is separated which, when mixed with hydrogen, deposits purified semiconductor-grade silicon (SeG-Si) on a heated seed rod. The process involves a complicated series of separation stages and recycle streams. Material balances for this process are summarized in the Appendix. Different assumptions concerning process loss may modify the estimates presented.[42]

Control Technology - Gases

A stream of gas, mostly carbon monoxide, carries off silicon monoxide and coke ash particles from the electric arc furnace. The gas may be burnt

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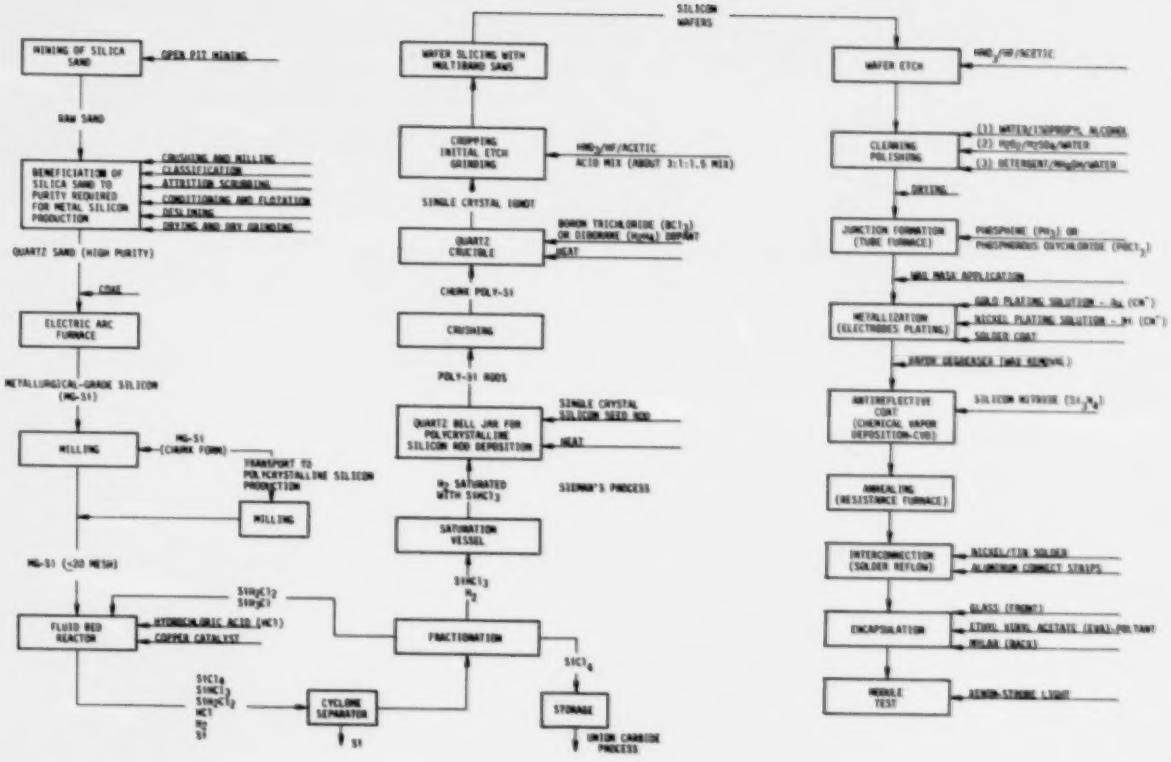

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Figure 3. Single-crystal silicon ingot process manufacturing steps.

Table 11
Pollutant emission rates from the production of silicon ingot photovoltaic cells

Activity	Process Step	Pollutant	Medium	(KG/Day*)/Plant	MT/YR)GWp
Silicon Production	Carbothermic Reduction of Silica	SiO as SiO_2	Vapor	1,377	48,180
		Ash	Vapor	33	1,140
		CO	Vapor	5,895	206,340
	Silicon Purification	Silicon dust loss from size reduction	Vapor	0.51 - 1.06	18 - 37
		Distillation bottoms ($SiCl_4$)	Liquid	1,160 - 2,000	40,600 - 70,000
		Non-condensibles (Hydrogen)	Vapor	283	9,900
		Vapor Dep. By-product (63% $SiCl_4$)	Liquid	8,753	306,370
	Silicon Purification by Union Carbide Process	Silicon dust loss from size reduction	Vapor	3.5	124
		Waste Settler discharge (79% $SiCl_4$)	Liquid	369	12,921
		Filter waste stream (43% H_2, balance chlorosilanes)	Vapor	38.6	1,351
		Stripper overhead (73% chlorosilanes)	Vapor	27.6	965
		Product Melter loss (Silane & hydrogen. Argon not incl)	Vapor	2.3	81
Cell Manufacture	Ingot Forming & Doping	Dust loss from crushing	Vapor	1.7	60
		BCl_3	Vapor	0.0009	0.031
		Crucible scrap (Si)	Solid	25.7	900
	Wafer Cutting & Etching	Silicon chips & dust	Solid	197	6,890
		Slurry (oil, clay & SiC)	Liquid	30.6	1,070
		Etching liquor (12% SiF_4 88% mixed acids)	Liquid	1,647	57,640
		Etching vapors (hydrogen rate given, but also some fraction of liquor vaporized)	Vapor	7.7	270
	Junction Formation	$POCl_3$ dopant	Vapor	0.0009	0.03
	Wafer Edge Grinding & Etching	Silicon dust (under water spray)	Liquid	1.7	61
		Etching liquor (mixed acids)	Liquid	(?)	(?)
		Etching vapors (SiF_4 and H_2)	Vapor	42.3	1480
	Electroless Plating & Soldering	Spent Ni plating solution	Liquid	85	2,990
		Acetone	Liquid	61	2,140
		Photoresist (urethane varnish and titanium dioxide)	Liquid	21 liters	[740 m^3]
		Rinse water	Liquid	28	1000
	Applicn. of Anti-Reflective Coating	Exhaust (60% HCl, 33% SiH_2Cl_2)	Vapor	0.15	5.2
		Si_3N_4 deposit on reactor walls	Solid	0.013	0.45
	Testing, Interconn., & Encap.	N E G L I G I B L E			

*Plant Capacity 10 MWp/yr., and 350 working days/yr.

in a waste heat boiler, and, for this reason, the dust must first be removed. Generally, a removal efficiency of 99% is desired. A dust collection system for this purpose may consist of a cyclone separator and a bag filter with an air-cooled heat exchanger in between, since the gas will leave the furnace at about 1000°C. However, it is more likely that an electrostatic precipitator (ESP) will be used. There are two reasons for this: (1) An ESP will not require the use of a heat exchanger and (2) an ESP can more efficiently remove the suspected submicron size SiO and ash entrained in the waste stream.

The remaining 1% of the dust will be carried through the waste heat boiler and out of the stack. The particulate control units will discharge through airtight valves to a common header, which may take a number of forms, depending on plant layout. If the dust collectors are set sufficiently high, dust conveying will occur by gravity; if not, either the dust must be elevated by some mechanical means or a pneumatic conveying system must be employed. There will be a number of discharges of waste particulates in such a plant, and a pneumatic system might well be used to handle all of them. It is probable that the silicon monoxide will be converted to silicon dioxide at the point of discharge into the atmosphere.

Combustion of carbon monoxide in waste heat boilers is a well-established technology, and no problems need be expected, except possibly from sulfur which may be present in the coke and pass to the boiler. Most of the sulfur in the parent coal will have been vaporized in the coke retort, and very little left in the coke. Dust will be carried off in the flue gas. The stream generation rate will depend on the pressure and temperature required.

Following carbothermic reduction, MG-Si must be ground fine in an air-swept mill before it is fed to the fluidized-bed chlorination reactor. The airstream will carry off MG-Si dust. This may pass through a bag filter, which will trap 99% by weight of the particles and discharge them to the plant dust-conveying system. The exhaust air will discharge dust to the atmosphere via a roof stack.

The purification plant uses hydrogen gas in the vapor deposition step, and recovers it from recycle streams in the separation and distillation step. The plant is close to hydrogen balance, but a bleed stream may have to be disposed of. It could be piped to the waste heat boiler and burnt with the carbon monoxide.

Control Technology - Liquids

There are two liquid emissions from this process. One is distillation bottoms, containing mostly tetrachlorosilane (or silicon tetrachloride), with possibly some heavy metal chlorides representing the heavy metals originally in the MG-Si. The other liquid emission is a by-product stream from the vapor deposition step consisting mainly of chlorides of silicon. The flows are of sufficient magnitude to be potentially valuable as feed materials to other processes. If not recycled, these materials will be burnt to recover muriatic acid (commercial grade hydrochloric acid), a useful by-product.

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Control Technology - Solids

Depending on the actual material balances, a residue may be left in the crucible of the electric arc furnace. This will be mostly silica with a large admixture of the impurities present in the quartz feedstock. This material will be stable and insoluble and can be simply landfilled. The only solid wastes generated during the refining of the silicon by the Siemen's process will be dusts recovered from the gas streams which may also be placed in a municipal landfill.

Hazard Potential

The types of pollutants present in the gaseous and liquid waste streams are not now identified as hazardous pollutants under the CAA and CWA. Waste streams (e.g., distillation bottoms) which contain a variety of acids, alcohols, chlorosilanes, and/or metal compounds are defined as "hazards" or "toxic" under RCRA guidelines and will have to be disposed of accordingly. If this waste stream is not combusted to produce muriatic acid, then it could be classified as a hazardous waste requiring controlled disposal.

PRODUCTION OF SEMICONDUCTOR-GRADE SILICON BY THE UNION CARBIDE PROCESS

Process Description

Union Carbide, under contract to the U.S. Department of Energy, is developing an alternative to the Siemens process now used to produce SeG-Si.[43] Like the Siemens process, the Union Carbide process requires chunk MG-Si of about 98% purity, produced by carbothermic reduction of silica. This material is fed to a mill, reduced to 120-μ average size, and conveyed pneumatically. Silicon feed is blended with a catalyst and stored under nitrogen, some of which bleeds off to a waste gas header.

Hydrogen gas conveys the prepared feed, together with recycle streams of silicon tetrachloride and hydrogen, to the hydrogenation reactor to produce trichlorosilane. The reacted stream proceeds to the waste settler, from which a waste stream is discharged to a liquid waste header. This waste stream contains most of the impurities in the silicon feed (as metal chlorides) and most of the silicon loss.

Product leaving the waste settler is cooled, the unreacted hydrogen is recycled, and crude trichlorosilane is run to buffer storage. From there, it is transferred to a stripper to remove light ends. En route, it is passed through a filter, from which another waste stream is taken. The light ends are removed overhead from the stripper, condensed, and returned as reflux, except for a gaseous stream discharged to a special waste gas header.

Subsequent processing of the trichlorosilane stream by means of stills and "redistributing" reactors generates a pure silane stream which is then pyrolyzed to pure silicon, and a silicon tetrachloride stream which is recycled to hydrogenation via buffer storage.

Control Technology - Gases

Like the Siemens process, the Union Carbide alternative requires that the MG-Si feed be ground fine. Dust will be carried off in the air sweeping the mill. A cyclone and/or bag filter will recover most of it, but a small, uncontrollable amount will be discharged to the atmosphere.

In the process of separating and redistributing the products of the hydrogenation reactor, two waste vapor streams will be combusted in a special burner to which natural gas will be fed to ensure that all chlorine is converted to hydrogen chloride. The combustion gases are cooled in a device which permits the silica particles formed in the combustion to agglomerate to form larger particles. The cooled gas passes through bag filters which remove most of the particles. Any remaining particles are removed by drawing the gas through a high-energy venturi, which is driven by medium-strength muriatic acid solution (i.e., impure hydrogen chloride). The gas, cleaned of solids, is then scrubbed free of hydrogen chloride in a two-stage venturi ejector, producing a nominally 20% muriatic acid. The scrubbed gases, cleaned of hydrogen chloride to parts per million levels, then pass through a muriatic tailing column, which has been packed with a sacrificial metal surface. The clean gas is exhausted to the atmosphere by a waste gas induction blower.

The purified silicon product has to be melted in preparation for the ingot-forming step. In the melting process, silane vapor plus some hydrogen will be released. Melting is done under an argon atmosphere, which subsequently dilutes the silane. The gas/vapor mixture is disposed of by burning.

Control Technology - Liquids

This process has one liquid waste stream, a waste settler discharge composed principally of various silicon compounds, which will be combusted to recover silicon and muriatic acid.

Control Technology - Solids

Depending upon the actual material balances, a residue will be left in the crucible of the electric arc furnace after carbothermic reduction. This will be mostly silica with a large admixture of the impurities present in the quartz feedstock. The material will be stable and insoluble and can be simply placed in a landfill. During purification no solid waste streams will be generated, with the possible exception of dust recovered.

Hazard Potential

Although large quantities of chlorosilanes may be produced, the waste streams will probably be combusted to form muriatic acid. If this waste stream is not combusted, controlled disposal will be required. No significant quantities of other hazardous waste are produced by this process.

MANUFACTURE OF SINGLE-CRYSTAL SILICON CELLS

Process Description

The manufacturing steps required to produce a single-crystal silicon cell are shown in Figure 3. As shown, SeG-Si must first be crushed and then cleaned with a mixture of trichloroethane, nitric acid, hydrofluoric acid, and water.[24]

The crushed silicon is melted in a crucible under an argon or helium atmosphere, and under slight vacuum. At this stage, the silicon is doped with boron by introducing either chunks of silicon containing the required amount of the element or a gaseous compound of boron, such as boron trichloride or diborane. The crucible and crystal are rotated in opposite directions while the crystal is withdrawn at a controlled rate to form a cylindrical ingot. Some scrap material will be left in the crucible, but it is clean and can be recycled to the purification plant.

The manufacture of wafers from the ingot requires a series of mechanical steps, each resulting in the removal of silicon: cropping the tapered ends of the ingot, grinding the ingot to the required diameter, and sawing the ingots into wafers. A slurry of equal parts by weight of oil, clay, and silicon carbide grit is used to saw the wafers, which then must be treated to remove saw damage. This is done by immersing them in a bath containing a mixture of nitric, hydrofluoric, and acetic acids.

In junction formation, phosphorus is diffused into the wafer surface by exposing the wafers to phosphorus oxychloride vapor in a furnace. Next, the wafer edges are ground under water sprays. Only a small quantity of silicon dust is removed. Then, the wafers are etched to remove the silicon dioxide layer formed during the diffusion process. The etchant consists of hydrofluoric acid either alone or in combination with nitric acid.

Metallization by electroless plating follows. Photoresist, a urethane varnish made thixotropic with titanium dioxide, is applied to a batch of wafers by squeegee over a screen made of stainless steel or plastic. Exposure to light fixes the resist. The wafers are then dipped sequentially into three baths: (i) a plating solution of nickel hypophosphite with some ammonia; (ii) acetone to remove the photoresist; and (iii) a water rinse bath.

The wafers are dried and sintered at 500°C under an atmosphere of nitrogen, then dipped in a flux bath (ventilated to remove chloride or formaldehyde fumes), followed by a solder bath (also ventilated). The wafers are finally washed with water, rinsed, and dried.

Silicon nitride is deposited on the wafers as an antireflective coating by chemical vapor deposition, using dichlorosilane and ammonia as deposition gases. Nitride is deposited, and hydrogen chloride and hydrogen are exhausted. Unreacted gases are also exhausted and some silicon nitride is deposited on the walls of the reactor. Cells are subsequently annealed in a

resistance furnace, tested, interconnected to form modules, encapsulated, and the modules are tested.

Control Technology - Gases

If ingot forming takes place in a separate facility, MG-Si will arrive in chunk form and must be ground before remelting. Sweeping the mill with air will carry off silicon dust. Use of the customary cyclone and/or bag filter will reclaim most of the dust, which is clean and recyclable.

Boron doping requires the introduction of boron into the melt. If this is done by injecting a boron compound such as boron trichloride, small quantities of unreacted boron trichloride, hydrochloric acid, and boric acid vapors will be lost. Melting is performed under slight vacuum, with an atmosphere of argon or helium. To maintain the vacuum, gas will be withdrawn continuously, carrying the waste streams with it. Contaminant concentrations will probably be extremely low.

After the ingot is formed and machined into wafers, the wafers must then be etched to remove saw marks and the oxide layer. Etching will be performed in an acid bath containing nitric, hydrofluoric, and acetic acids. A ventilation hood will extract vapors in an airstream, which will then pass up a scrubbing column. The vapors will contain all three acids plus silicon tetrafluoride. The scrubber liquor will be lime slurry, which will react with the hydrofluoric acid and silicon tetrafluoride to produce calcium fluoride, a solid of low solubility. Spent scrubber liquor will be piped to a neutralizing pond for settling. Pond effluent will run to a retention lagoon for periodic analysis and discharge.

For phosphorus doping, phosphorus oxychloride may be used as the diffusion gas. It is expected that small quantities of this compound, including possible breakdown products (phosphoric anhydride, hydrogen chloride, etc.), will be lost to the ventilation system. An extraction fan of suitable capacity will ensure that the pollutant concentration will comply with regulations, or scrubbing with a suitable liquor can be employed. The wafer edges are next cleaned by grinding under water sprays. This is clean material, and collecting the spray in a settling tank will permit the recovery of silicon. Another etching stage will use nitric and hydrofluoric acids. Some of this, again, will remain in solution, but some will be carried off by ventilating air, which will also remove nitric and hydrofluoric vapors. This stream can be treated in the same lime scrubber as the previously described stream.

Following etching, the wafers are subjected to plating and soldering. No exotic materials are employed, but ventilation will be provided for ammonia (plating bath), acetone (photoresist removal), flux vapors (chloride or formaldehyde fumes), and solder fumes.

Silicon nitride is deposited on the wafers as an antireflective coating by chemical vapor deposition. A small loss of reactants and products takes place, of which the greater part by far is hydrogen chloride gas and

dichlorosilane. Scrubbing with dilute hydrogen chloride will yield a small stream of muriatic acid, which can be dumped into a neutralizing pond.

Finally, wafers are tested, interconnected into modules, and encapsulated. Ventilation will be required to remove flux and solder fumes and the odor of heated plastic.

Control Technology - Liquids

After ingot formation, the ends are cropped and the ingot diameter is reduced to a standard size. Then the ingot is cut into wafers. During the sawing operation, the ingot is cooled by spraying the saw blades with a cutting compound consisting of clay, oil, and silicon carbide grit. A large fraction of the silicon is discharged with the slurry. The silicon may be worth separating from the slurry, but it will probably be too finely divided. Spent slurry containing the silicon kerf is run to a settling tank to permit skimming off the oil. The accumulated solid material will be periodically removed, drained, and placed in a landfill.

Cell manufacture requires two etching steps. The first results in a discharge stream containing tetrafluorosilane, nitric acid, hydrofluoric acid, and acetic acid. The second etching tank discharge stream is chemically similar to the first, but without the acetic acid. Both streams are pumped to the neutralization pond and neutralized with lime. The sludge from the pond will need to be placed in a secure landfill. The supernatant liquid will contain nitrates and fluorine. Disposal options, including biological denitrification, require further analyses.

Metallization of the cells requires the disposal of several liquid streams. First is a spent nickel plating solution containing ammonia and wetting agents. Flocculation is generally used. This will require a pH of 11 or 12, rather than the usual 9 or 10, this may require additional lime.

Another liquid requiring disposal is the acetone in which the cells are dipped after plating to remove the photoresist mask applied to the cells before plating. In this application, the acetone is said to be nonrecoverable. A recoverable solvent could be collected in a storage tank and recovered, perhaps one day each week in a small batch still. The residue could then be added to the plant's fuel oil.

Finally, the cells are rinsed in a water bath. To reduce contaminant pickup, the cells coming from the acetone or solvent rinse could be run through a "squeegee" device to remove excess liquid. To reduce water consumption, sprays could be substituted for the bath.

Control Technology - Solids

In the process of machining ingots to size and sawing them into wafers, contaminated silicon will be discharged with the slurry. This material may be treated as liquid or solid waste (see Control Technology-Liquids).

Another solid waste generated in the application of the antireflective coating will be silicon nitride deposited on chamber walls and equipment. It can be removed by hand periodically, placed in drums, and deposited in a landfill.

Hazard Potential

Promulgated NESHAP do not apply to pollutants emitted by this process. Under the CWA, reporting requirements exist for fluorides, and copper, nickel, silver, and degreasing agents are defined to be toxic pollutants. Standards developed for each of these pollutants ultimately need to be complied with. RCRA identifies wastes from degreasing and electroplating operations to be hazardous. Fluorine, nickel, nitric acid, and phosphine are also listed as "Acute Hazardous Wastes," and acetone, degreasing agents, and hydrofluoric acid are listed as "Toxic Wastes." Thus, solid wastes generated by this industry will probably be declared hazardous if large quantities are produced and require disposal in controlled landfills. Initial estimates displayed in Table 11 suggest that the 1000 kg/month standard may be exceeded for three effluent streams: the etching liquors from the wafer slicing and wafer edging, and spent plating solution from electroless plating. Estimates of effluent quantities from other process steps indicate that they will not surpass this RCRA threshold value.

SECTION 8

PRODUCTION OF SEMICRYSTALLINE SILICON RIBBON PHOTOVOLTAIC CELLS

The refining and manufacturing steps required to produce a semicrystalline silicon ribbon photovoltaic cell are shown in Figure 4 and related emissions are displayed in Table 12. Like the single-crystal silicon ingot photovoltaic cell, this cell requires semiconductor-grade silicon. Silicon produced by either the Siemens or the Union Carbide process is used and, therefore, the reduction and purification steps are not reexamined. Note, however, that the silicon demands are lower for this process than for single-crystal ingot growth. Thus, refining emissions per unit production are lower by a factor of about 2.6.

MANUFACTURE OF SEMICRYSTALLINE SILICON RIBBON PHOTOVOLTAIC CELLS

Process Description

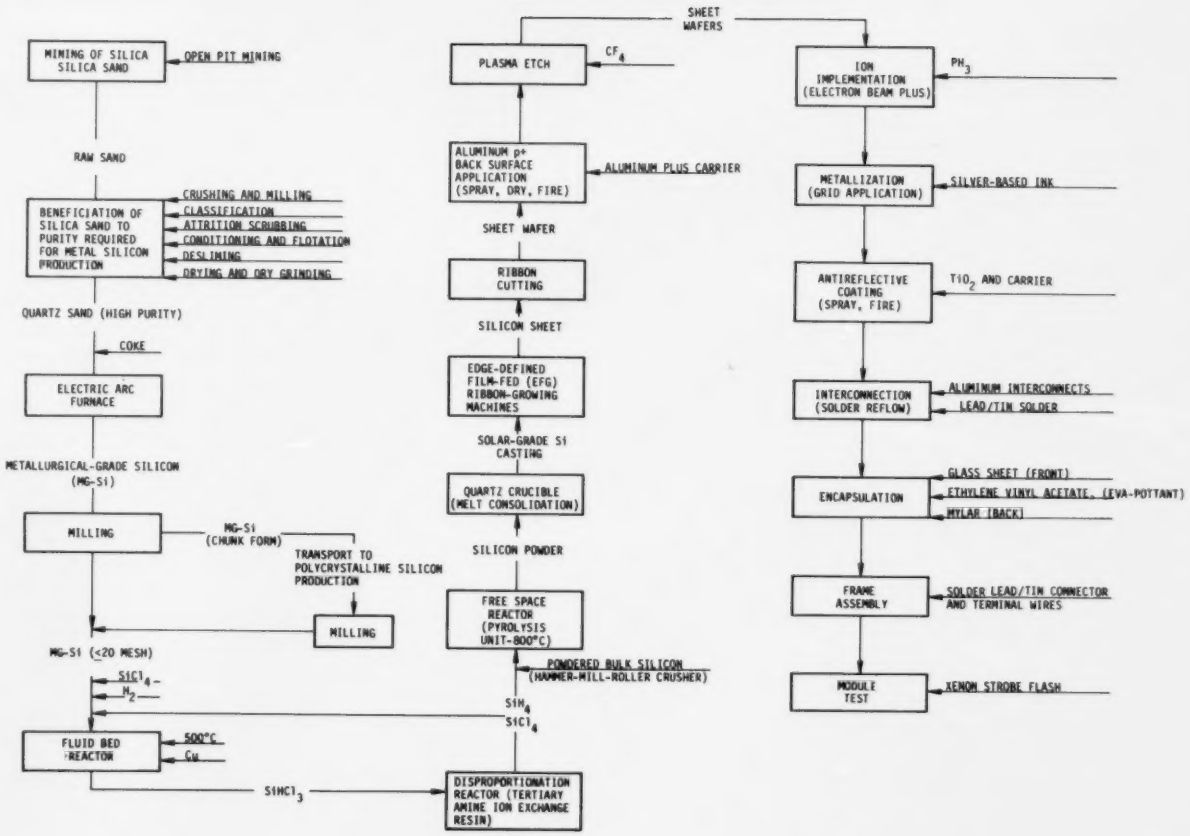
Production of silicon ribbon cells begins with the melting of semiconductor-grade silicon inside a graphite die. Inside the die, capillary action causes the melted material to rise. At the top of the die it solidifies in contact with a seed of silicon, which is then drawn upward at a rate such that the molten silicon continues to cool in the die and subsequently generates a semicrystalline ribbon.

The solidified ribbon is scribed and cut into wafers. The cut wafers are delivered to a machine in which they are sprayed with a slurry of aluminum powder in ethanol, after which they pass through ovens where they are dried and fixed.

The fixed wafers are transferred to a reaction chamber, in which a slight vacuum is applied, and an etchant gas is introduced to remove silicon dioxide. The gas is 8.5% oxygen and 91.5% carbon tetrafluoride; radiofrequency energy is applied to generate active gas species. Reaction products are removed by a vacuum pump, and may include silicon tetrafluoride, silicon oxyfluorides ($SiOF_2$, Si_2OF_6), oxygen, fluorine, and carbon dioxide.

Etched wafers are next conveyed to the ion implantation step. Phosphine gas mixed with hydrogen is used as the phosphorus source. The process is also performed under vacuum.

Wafers are sequentially metallized, first on the back, then on the front. A silver-based ink is applied by squeegee over a screen to print the



Source: Reference 26.

Figure 4. Semicrystalline silicon ribbon process manufacturing steps.

Table 12
Pollutant emission rates from the production of silicon ribbon photovoltaic cells

Activity	Process Step	Pollutant	Medium	(kg/Day*)/Plant	(MT/YR)/GWp
Silicon Production	Carbothermic Reduction of Silica	SiO as SiO_2	Vapor	524	18,344
		Ash	Vapor	12.4	434
		CO	Vapor	2,245	78,560
	Silicon Purification by Siemens Process	Silicon dust loss from size reduction	Vapor	0.2 - 0.4	7 - 14
		Distillation bottoms ($SiCl_4$)	Liquid	442 - 761	15,460 - 26,650
		Non-condensibles (Hydrogen)	Vapor	108	3,770
		Vapor Dep. By-product (63% $SiCl_4$)	Liquid	3,333	116,650
	Silicon Purification by Union Carbide Process	Silicon dust loss from size reduction	Vapor	1.3	47
		Waste Settler discharge (79% $SiCl_4$)	Liquid	141	4,920
		Filter waste stream (43% H_2, balance chlorosilanes)	Vapor	14.7	514
		Stripper overhead (73% chlorosilanes)	Vapor	10.5	367
		Product Melter loss (silane & hydrogen argon not incl)	Vapor	0.9	31
Cell Manufacture	Melting, Ribbon Forming & Cutting	N E G L I G I B L E			
	Back-Contact Application	Al-Ethanol slurry (5% Al by weight)	Liquid	230	8,063
		Ethanol vapor (diluted with air)	Vapor	94	3,290
	Plasma Etch	Exhaust via vacuum pump (SiF_4 & oxyfluorides)	Vapor	S M A L L	
	Ion Implant	Exhaust (Phosphine and hydrogen. Dilute air rate not given)	Vapor	0.0008	0.027
	Metallization	Ag ink (Vehicle not known)	Liquid	51.2	1,793
		Vaporized vehicle	Vapor	(?)	(?)
		Cleaning solvent	Liquid	(?)	(?)
	Antireflective Coating	TiO_2 spray (Vehicle not known)	Liquid	1.5 liters	[53.6M^3]
		Vaporized vehicle	Vapor	(?)	(?)
		Cleaning solvent	Liquid	(?)	(?)
	Testing, Interconn., & Encap.	N E G L I G I B L E			

*Plant Capacity 10 MWp/yr, and 350 Working days/yr.

pattern, and the wafers are then dried and sintered at 550°C. Excess ink is disposed of either when the screen is washed off with solvent, or when the screen itself is disposed of.

Finally, the wafers are sprayed with an antireflective coating of titanium dioxide carried in a liquid vehicle. The coated wafers are then dried and baked. It is estimated that 30% of the spray coats the wafers, and the vehicle of this fraction is evaporated during drying. The remaining 70% ends up on equipment and chamber walls and is removed by solvents.

Cell testing, interconnection, encapsulation, and module testing are essentially emission free.

Control Technology - Gases

If ribbon forming takes place in a facility separate from the refinery, then SeG-Si will arrive in chunk form and must be ground before remelting. Sweeping the mill with air will carry off silicon dust. Use of the customary cyclone and/or bag filter will reclaim most of the dust, which may be clean and recyclable.

Melting, ribbon forming, and ribbon cutting are essentially emission-free operations, a negligible amount of dust arising from cutting the ribbon into wafers. Application of back-contact is by spraying the wafers with aluminum powder slurried in ethanol and drying in ovens under a high-capacity air exhaust system. The airstream will carry away aluminum powder and ethanol vapor. Passing the hot stream through a cyclone/bag filter system will recover all but approximately 3% of the powder. Following this, a chilled heat exchanger will condense much of the ethanol, which will also bring down some of the remaining powder. The resulting liquid can be recycled to form fresh aluminum slurry.

Plasma etching is performed under a slight vacuum. The reaction products are removed by a vacuum pump and include silicon tertrafluoride, silicon oxyfluorides, fluorine, and carbon monoxide. The quantities are expected to be small. The stream will be absorbed in a lime scrubber, and spent liquor will be discharged to the neutralizing pond.

Ion implantation follows, with small emissions of phosphine and hydrogen expected. These will be removed in an air exhaust system of sufficient capacity to give a diluted discharge.

Wafers are metallized using a silver ink. The operation is performed under a high-capacity air exhaust system. The composition of the ink is proprietary information, and the nature of the vehicle is unknown. It is presumed that vaporized vehicle, together with some finely divided silver, will be carried off in the exhaust air. Some degree of recovery will probably be obtained by the methods described above for aluminum slurry.

Titanium oxide, in some proprietary liquid vehicle, is then sprayed on the wafers to form an antireflective coating. Excess liquid will be disposed of in a manner similar to that of the ink applications.

Finally, wafers will be tested, interconnected into modules, and encapsulated. All that is required is ventilation to remove flux and solder fumes and the odor of heated plastic.

Control Technology - Liquids

Solvents will be required to clean silver ink splatter and titanium dioxide splatter from chamber walls and equipment. The resultant washings may be recycled.

Control Technology - Solids

The solid residues left by the silver ink and titanium dioxide sprays may have useful metal values. Dried splatter will probably be scraped, placed in drums, and shipped off for recovery.

Hazard Potential

Although the waste stream from the metallization step is likely to be recycled, presence of silver compounds may result in a classification of this waste stream as toxic or hazardous. Additional controls may be required.

SECTION 9

PRODUCTION OF CADMIUM SULFIDE/COPPER SULFIDE CELLS

The cadmium refining and subsequent manufacturing steps required to produce a backwall cadmium sulfide photovoltaic cell by a spray deposition process are shown in Figure 5. Process descriptions and control technology needs are described below. In Table 13, process emissions on a per plant and per unit production basis are given.

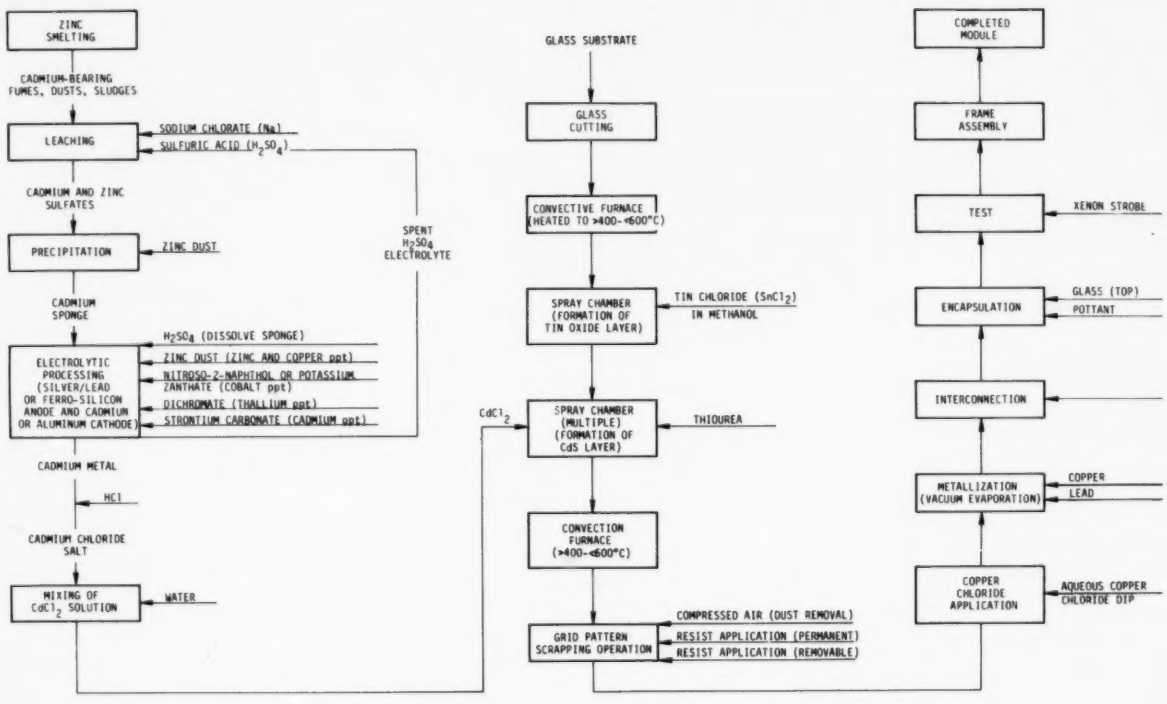
PRODUCTION OF CADMIUM CHLORIDE

Process Description

Cadmium metal is recovered from the wastes of zinc refining as a sponge of about 99.5% purity. The cadmium is purified to 99.995% purity by a process known as electrowinning. In this process, a cadmium sponge is oxidized to cadmium oxide with steam, and the resulting material leached with spent electrolyte and sulfuric acid to generate new electrolyte, i.e., an aqueous solution of cadmium sulfate. The solution is filtered, and impurities are precipitated with a strong oxidizing agent, such as manganese dioxide. These impurities constitute the difference between 99.5% purity and 99.995%. They include some, or all, of the following: arsenic, thallium, lead, iron, and copper. The precipitate is filtered out, and the oxidizing agent remains in solution as sulfate. Animal glue is added to enhance the smoothness of the cadmium cathodes obtained by electrolysis. The cathodes are removed every day, rinsed, and stripped. The stripped cadmium is melted and cast into shapes. Cadmium chloride can be produced by direct reaction of the metal with chlorine gas or hydrogen chloride gas. It can also be produced in solution by reacting the metal with aqueous hydrogen chloride. Since it is required as a solution in the cadmium sulfide deposition step, the second method would appear to be more appropriate. The literature does not identify the specific process employed.

Control Technology - Gases

Electrowinning is a liquid process requiring only ventilation hoods and air exhaust fans. Production of cadmium chloride, as herein described, is also a wet process, but hydrogen is generated and proper ventilation is important. Proper-sized air exhaust systems will ensure that the spontaneous combustion concentration is never reached.



Source: Reference 26.

Figure 5. Cadmium sulfide/copper sulfide process manufacturing steps.

Table 13
Pollutant emission rates from the production of cadmium sulfide/copper sulfide

Activity	Process Step	Pollutant	Medium	(kg/Day*)/Plant	(MT/YR)/GWp
Production of CdS-Coated Substances	Electrowinning	Heavy metal precipitate (as FeO)	Solid	0.11	3.90
		Spent electrolyte Conc. unknown but containing the following quantities of	Liquid		
		$CdSO_4$		0.42	14.65
		$Mn(SO_4)_2$		0.39	13.63
	$CdCl_2$ Production	Hydrogen	Vapor	0.3	10
	Processing of Glass Substrates	Exhaust (mostly methanol vapor, containing some formic acid HCl, & $SnCl_2$. Dilutant air rate not given.)	Vapor	16.1	562.4
	CdS Applicn	Exhaust (60% thiourea, 35% breakdown products. Rest is $CdCl_2$. Dilutant air rate not given.)	Vapor	9.6	336†
Cell Manufacture	Grid Forming	CdS dust	Solid	0.06	2
		SnO vapor (Dilutant air rate not given)	Vapor	0.02	0.6
	Cu Ion Implant	Plating solution containing 20 mg/l Cu and 18 mg/l Cd	Liquid	128 liters	[4,473 m^3]
		Deionized water rinse	Liquid	(?)	(?)
	Metallization	Metals deposited on vacuum chamber walls:	Solid		
		Copper		5.9	207
		Lead		21.5	753
		Unknown metal		(?)	(?)
	Testing, Interconn. & Encap.			N E G L I G I B L E	

*Plant Capacity 10 MWp/yr, and 350 Working Days/yr.
†It has been estimated that 952 MT/yr of cadmium are released to the atmosphere by ore refining processes.

Control Technology - Liquids

In the electrowinning process for purifying cadmium metal, a spent acidic solution containing unknown concentrations of cadmium sulfate and manganese sulfate is discharged. The discharge will be treated by adding lime to neutralize the acid and precipitate the heavy metals. Manganese will require a pH >10.

Control Technology - Solids

In preparing an electrolyte for the electrowinning of pure cadmium, a precipitate of the oxides of heavy metals is filtered off, which could be recycled or collected, placed in drums, and disposed of in a controlled toxic and hazardous waste landfill.

Hazard Potential

Discussions with EPA officials suggest that cadmium will not be declared a hazardous pollutant.[39] Under the CWA, cadmium, copper, cyanide, nickel, silver, and degreasing agents are all classified as "toxic" pollutants. Standards developed for these pollutants will require compliance. Similarly, under RCRA, degreasing agents and cadmium compounds will need to be placed in controlled landfills if quantities exceed 1000 kg/month. This analysis, however, suggests that this standard will not be exceeded.

MANUFACTURE OF CADMIUM SULFIDE/COPPER SULFIDE CELLS

Process Description

Precut glass wafers are washed and air dried, and then heated in a radiant oven and sprayed with a solution of tin chloride in methanol. In contact with the hot glass, the tin chloride and methanol react to form tin oxide, which is deposited in a film 0.5 μ thick.

Next, aqueous solutions of thiourea and cadmium chloride are sprayed onto the heated glass substrate. These react to deposit a layer of cadmium sulfide 4.0 μ thick.

After this step, grid patterns are marked on the substrate by a needle-shaped instrument which mechanically scrapes off the cadmium sulfide down to the tin oxide layer. The exposed tin oxide is then vaporized by a laser beam. After the glass substrate is exposed, two layers of resist are laid down by pens. In the next step, two copper ions replace each cadmium ion in the surface of the cadmium sulfide layer. This is done by passing the cells through a series of tanks containing a proprietary copper chloride solution. Elsewhere, the solution is identified as saturated. Presumably, the solution contains other solutes beside copper chloride, but these are not known.

After ion exchange, cells are rinsed in deionized water. Metallization is carried out in a vacuum chamber and pellets of three metals are evaporated in sequence, 35% depositing on the cells. The rest is deposited on the vacuum chamber walls and fittings, or removed through the vacuum system. Copper is laid down to a thickness of 0.7 μ, followed by 2.0 μ thickness of lead. The third metal is proprietary.

Subsequent assembly steps include interconnection, encapsulation, test, and frame assembly.

Control Technology - Gases

Tin oxide coating is applied by spraying heated gas wafers with a solution of tin chloride in methanol. Emissions from this process will be carried away in an exhaust airstream, which will flow through a baghouse to allow recovery of the powder, and then into a water scrubber. Approximately 97% will be recovered and shipped for tin recovery. The remaining 3% will

be lost to the scrubber liquor, which will be piped to the neutralization pond.

Spray deposition of cadmium chloride/thiourea is physically similar to the previous operation, with the air exhaust system sweeping away unreacted cadmium chloride and thiourea, water vapor, and reaction products. Of particular concern is the potential for production of HCN. The discharged air will be fed to a baghouse to recover cadmium chloride and then to a water scrubber. Spent scrubber liquor will be piped to the neutralization pond.

In order to lay down a metallized grid on the glass wafer, the coatings of cadmium sulfide and tin oxide must be removed. The former is removed mechanically by needles, and the dust so formed is vacuumed away. The latter is removed by volatilization with a laser beam. The tin oxide fumes, which are minor, will be carried away by an air exhaust system and discharged to the atmosphere through a roof stack. Other process steps also require adequate ventilation, i.e., the plating baths used for copper ion implantation, flux and solder fumes from module assembly, and heated plastic vapors from encapsulation.

Control Technology - Liquids

A spent plating solution containing the chlorides of copper and cadmium is discharged from the copper ion implantation process. Other compounds may be present, but such information is proprietary. This solution will be treated by flocculation to reduce the metal concentrations.

Control Technology - Solids

Before placing a metallized grid on the glass wafer, the cadmium sulfide coating must be removed to form the desired pattern. This is done mechanically by needles, and cadmium sulfide dust will be removed by vacuum cleaner and deposited in drums for shipping to a recovery plant or to a secure landfill.

Metallization of cells is carried out in a vacuum chamber, and pellets of three metals are evaporated and deposited in sequence. Some of the metal is deposited on the vacuum chamber walls and fittings and must be removed by hand periodically. The metal sequence is copper, lead, and an unknown metal (possibly Inconel). The mixture may be of value for recovery purposes; otherwise it must be placed in a secure landfill.

Hazard Potential

Cadmium discharges into any medium will come under careful review. Under the CWA and RCRA, these wastes may be declared "toxic" or "hazardous" and require specific control. Release of cyanides and thiourea may also be controlled under authorities of the CWA and RCRA. Quantities of these pollutants to be discharged, however, are not expected to be large.

SECTION 10

INSTALLATION

Photovoltaic energy systems may be used in either decentralized or centralized applications. Environmental effects related to decentralized applications are not significant and are therefore not discussed. Central-station installation effects relate to construction activities and land use requirements.

Ground-mounted central-station photovoltaic systems require about 2 ha/MWp or ~3 km^2/100 MWp.[32] Lands most suitable for central-station applications lie in the southern portions of the United States where annual insolation is high.[43] Other factors, such as regional energy demand and proximity to population centers, however, will effect ultimate siting decisions.

Effects from installation relate principally to site cleaning and preparation activities.[14,15,25,31] Dust generation associated with the concomitant destruction of the desert crust which protects the finer lower layers from wind and rain are issues of general concern.[31,32,45,46] Disruption of the crust could also lead to increased erosion from water and wind. Use of heavy vehicles may also cause soil compaction which could affect burrowing animals and infiltration of water.[46,47] Reduced infiltration, in turn, may affect plant growth, runoff, and subsurface hydrogeology.[45] Some ecologists believe that effects from soil compaction may be irreversible. The magnitude of these effects will depend upon the construction techniques employed and site characteristics.

SECTION 11

OPERATION AND MAINTENANCE

Effects from operation and maintenance relate to active requirements for site and panel maintenance, and indirect modifications to the micro- and meso-scale erosion proximate to the array field. Aside from small quantities of water used for periodic cleaning of the photovoltaic panels, and herbicides used to reduce plant growth in proximity to the arrays, photovoltaic systems will operate noiselessly and without pollution.

In contrast with conventional systems, most operational effects probably relate to shading, wind deflection, and soil compaction. Soil erosion and albedo will initially be high because of vegetation removed and soil compaction. Panel shading and wind deflection will produce a variety of micro-climatic changes, including decreased air, surface, and soil temperature; decreased evaporation or increased soil moisture; decreased land wave radiation; and decreased wind. These modifications may affect species diversity and standing biomass in ecosystems located proximate to the array field.[32,44-46]

It has been suggested that meso-scale climatic effects of very large facilities (>5 km^2) may be considerable, although their significance has not been quantitatively evaluated. Installation of photovoltaic panels may cause significant changes in the surface albedo, roughness, porosity, emissivity, thermal conductance, heat capacity, and the remission ratio. Changes in these characteristics could create local variations in wind, temperature and humidity.[25,50]

SECTION 12

DECOMMISSIONING

Large-scale disposal of spent photovoltaic devices will occur ~20 to 30 years after their initial installation. In decommissioning, the principal concern will be disposal of solid wastes, including spent photovoltaic panels, controllers, circuitry, and supports. These materials may either be landfilled or possibly recycled. Most of the solid waste will be nonhazardous, but spent cadmium sulfide/copper sulfide photovoltaic cells (0.6MT/MWp) may be defined as hazardous and require disposal in controlled landfills. For comparison, note that ~2000 MT of cadmium waste are presently disposed of in landfills.[51] Disposal of these devices by a utility from a large-central station or utility-controlled decentralized grid will be facilitated, but disposal by individual homeowners of small domestic units may be difficult to monitor. Materials disposed of by the homeowner could end up being incinerated in a municipal system, with small quantities of this toxic material being released to the atmosphere. Alternatively, materials may be deposited in municipal landfills where cadmium could be leached into groundwater systems and possibly into the food chain.

For central-station applications, land used will probably be maintained by utilities for similar applications. Spent devices will simply be replaced. Thus, site restoration will not be required.

SECTION 13

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Appendix A

ESTIMATES OF EMISSIONS PER UNIT PRODUCTION FOR THE PHOTOVOLTAIC INDUSTRY

INTRODUCTION

Emission rates for the various process steps in photovoltaic cell manufacture are discussed in this appendix. The rates given herein are generally reported in units of metric tons per megawatt (MT/MWp), unless the flows are so small that it is more convenient to report them in kilograms per megawatt (kg/MWp). In the case of the Union Carbide process for silicon purification, emission rates are given in metric tons per year (MTY), because the source of the information was a preliminary plant design with a capacity of 1000 MTY of pure silicon.

The latter capacity represents 78 MWp/yr for cell manufacture from ingots, and 204 MWp/yr for cell manufacture from ribbon. Conversion to the 1 GWp/yr base (see Tables 11, 12 and 13) therefore required multiplication by factors of 1000/78 and 1000/204, respectively. For those rates given in MT/MWp or kg/MWp, conversion to the 1 GWp/yr simply required multiplication by 1000. In a few instances, liquid flow rates were given in cubic meters per MWp (m^3/MWp). Conversion was again simple multiplication by 1000.

Since one purpose of this report was to explore the treatment technology available for handling these emissions, it was felt that it would be more useful to report emission rates on a daily basis. Furthermore, it is expected that a number of plants will be engaged in each manufacturing step, and an estimate of the daily emissions per plant would be useful. Obviously, at this time, the number of plants, and their respective sizes in the future are not known. However, a plant capacity of 10 MWp/yr of cells was considered reasonable. Multiplying the emission rates for 1 GWp/yr production by a factor of 1000/100 yielded the plant emissions in kg/yr. Assuming further that plants would operate for 350 days each year (to account for sceduled and unscheduled shutdowns), division by 350 then gave plant emission rates in kg/day.

The discussion in this appendix, and in the body of the report, considers three categories of emissions: gas stream, liquid, and solid. Gas streams include any emission involving a gas or vapor, or exhaust gas streams carrying dusts. It is to be understood that these characterizations refer to the actual point of discharge from the process, since, in the course of treatment and disposal, these streams are likely to be converted from one medium to another. Pollutants in a gas stream, for example, might be removed by scrubbing with a liquid, and thus yield a liquid disposal

problem. Another example would be the precipitation of heavy metals from a liquid emission, which would lead to a solid disposal problem.

PRODUCTION OF METALLURGICAL-GRADE SILICON BY THE CARBOTHERMIC REDUCTION OF SILICA

In this process, quartz is mixed with coke in an electric arc furnace, which is heated to 1000°C. The carbon in the coke reduces the silica of the quartz to elemental silicon, forming carbon monoxide in the process. The silica contains impurities, as does the coke. The products are a silicon containing 2 to 3% of heavy metals, a gas consisting mostly of carbon monoxide but with impurities arising from volatile contaminants in the coke, and a dust containing ash and silicon monoxide. The silicon product is called metallurgical-grade silicon (MG-Si).

Manufacturing details of the process are proprietary, but Owens et al.[1] have marshalled the available information and have determined that the ingot process for manufacturing silicon photovoltaic cells requires 89.9 MT/MWp of MG-Si, which is obtained from 245.4 MT/MWp of quartz and 94.2 MT/MWp of coke. They also identify, as losses, 35.3 MT/MWp of SiO and 1.15 MT/MWp of ash.

Earlier, with essentially the same information, Gandel et al.[2] drew up a flowsheet for the process, using "handbook" assumptions. They start with the same quantities of quartz and coke, but further characterize the quartz as 98% SiO_2 (the balance being metal oxides) and the coke as 91.8% carbon, 1.21% ash, and the remainder sulfur, hydrogen, nitrogen, and oxygen. From this feed, they derive a MG-Si product of 92.58 MT/MWp, containing 97% Si (89.9 MT/MWp), the rest being metals. Their dust discharge is approximately the same,[1] and the gaseous product is 206.34 MT/MWp, being 97.78 wt % CO. Their material balance shows a shortage of oxygen, but if this were made up by air the additional nitrogen should show up in the gas composition, which it does not. Furthermore, no allowance is made for crucible scrap. However, crucible scrap, if it exists, would be an innocuous crude quartz, easy to dispose of.

For purposes of estimating uncontrolled emissions, the following numbers are used:

a) Dust emissions

SiO	35.35 MT/MWp,
Ash	1.14 MT/MWp,

b) Gaseous emissions

Impure CO	206.34 MT/MWp.

The SiO and ash emissions will come off together, and, since the SiO can be expected to oxidize rapidly to SiO_2, the material will be a very fine and dirty sand, with a total weight of (48.18 + 1.14) = 49.32 MT/MWp. All the above numbers are for the production of silicon cell wafers from ingot

stock. For producing silicon ribbon, only 5.20 MT/MWp of MG-Si is required.[1] Therefore, these numbers must be reduced in the ratio 5.20:89.0.

PRODUCTION OF SEMICONDUCTOR-GRADE SILICON FROM METALLURGICAL-GRADE SILICON BY THE SIEMENS PROCESS

Finely ground MG-Si is reacted with hydrochloric acid, forming a mixture of related compounds. From this mixture, a stream of trichlorosilane is separated, which, when mixed with hydrogen, deposits purified semiconductor-grade silicon (SeG-Si) on a heated seed rod. The process involves a complicated series of separation stages and recycle streams. It is self-sustaining in hydrogen,[2] even, apparently, providing a small surplus to be disposed of.

Owens et al.[2] indicate that two stages of size reduction are employed to produce a MG-Si stream of the needed fineness. First, the crystallized product from the reduction stage is crushed into chunks, and second, the chunk material is milled into powder. A loss of 2% is said to occur at each stage. On the other hand, Gandel et al.[2] show only one stage of size reduction, but also estimate a 2% loss. Thus, dust emissions from size reduction run 1.80 to 3.70 MT/MWp.

In the reaction stage, the powdered MG-Si (<20 μ in size) is fluidized by hydrochloric acid gas. Gandel et al.,[2] with a slightly higher MG-Si feed, use less HCl (344.8 MT/MWp) than Owens et al.[1] (375 MT/MWp). Both agree on the quantity of $SiHCl_3$ leaving the separator: 371 MT/MWp. Owens et al. do not specify the emissions up to that point, but a material balance indicates emissions totalling 90.3 MT/MWp (see Figure A-1).

It is not realistic to attempt to quantify random drips, drains, and leaks. These are a function of the proper selection of construction materials and good housekeeping. We must, however, definitely remove distillation bottoms, and noncondensibles should be vented on a controlled basis, for the proper operation of condensers in the separation system. Gandel et al. confirm the latter point, and indicate a vent stream of 9.9 MT/MWp of hydrogen. They also indicate a distillation bottoms stream of 40.58 MT/MWp of pure $SiCl_4$. This process scheme is perhaps oversimplified. One would expect the bottoms to contain at least a small fraction of lighter materials. As for the impurities in the MG-Si, these could carry through into the still bottoms. However, Gandel et al. pass the reactor vapor product through a cyclone separator and indicate that the impurities in the MG-Si drop out there as metals which have failed to react with the HCl. They identify these as Ti and Al. One presumes that the Al, at least, would have reacted.

The emissions from the reaction and separation steps can be tentatively identified as follows.

a) Dust loss from size reduction — 1.80 to 3.70 MT/MWp - MG-Si, 97% Si.

b) Still bottoms — 40.6 to ~70 MT/MWp - mostly $SiCl_4$.

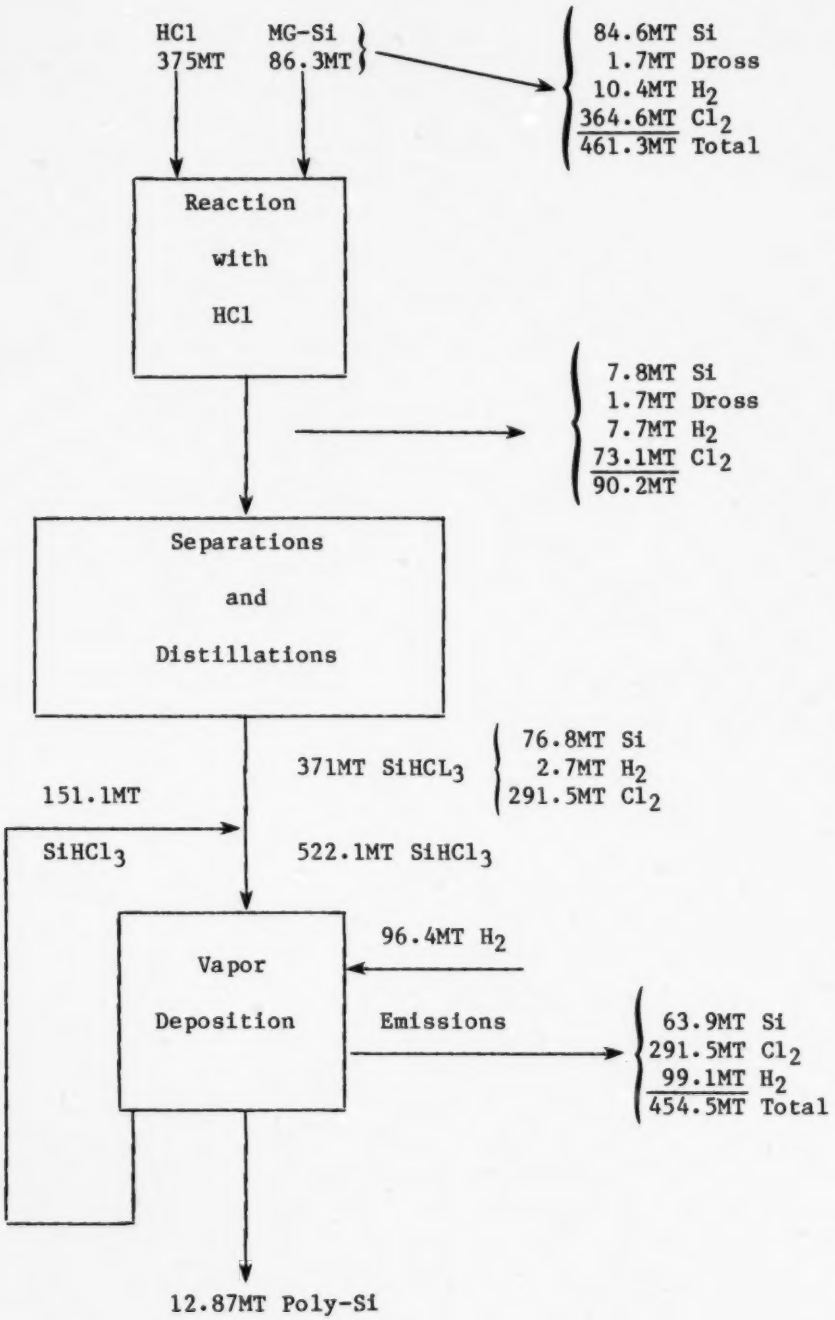

Figure A-1. Material balance for Siemens Process for semiconductor-grade silicon. Per Owens et al.[1]

The material balances differ for the two information sources cited.

c) Noncondensibles 9.9 MT/MWp - hydrogen.

d) Impurities in MG-Si 5.96 MT/MWp - impurities.

The quantity shown is a stream removed from the reactor product stream, and includes unreacted silicon (56% Si).

Proceeding now to the deposition stage, the feed streams are 371 MT/MWp of $SiHCl_3$ and 96.4 MT/MWp of H_2. The product stream is 12.87 MT/MWp of SeG-Si, which, by difference, yields a total waste stream of 454.53 MT/MWp. Both Owens et al. and Gandel et al. agree closely on this number. The latter, however, break this total down as follows:

a) By-product stream

SiH_2Cl_2	112.68 MT/MWp
$SiHCl_3$	0.29 MT/MWp
$SiCl_4$	193.40 MT/MWp
Total	306.37 MT/MWp

b) HCl, recycled to the reactor
49.97 MT/MWp

c) H_2, almost all recycled to vapor deposition
96.96 MT/MWp

The above emission rates were based on manufacturing cells from ingot. For manufacture from ribbon, these numbers must be reduced in the ratio 4.9:12.87.

PRODUCTION OF SEMICONDUCTOR-GRADE SILICON FROM METALLURGICAL-GRADE SILICON BY THE UNION CARBIDE PROCESS

The following process description is based on information published by Union Carbide for a plant designed for a capacity of 1000 MT SeG-Si per year (MTY).[7] For the ingot process, 12.87 MT are required per MWp,[1] so that, for this purpose, 1000 MTY is equivalent to about 78 MWp/yr. On the other hand, for the ribbon process, 4.9 MT are required per MWp[1]; thus 1000 MTY represents 204 MWp/yr. The quantities presented in this section will be based on the production rate of 1000 MTY of SeG-Si.

Chunk metallurgical-grade silicon of 98% purity is fed to a mill, and reduced to 120-μ average size. The feed rate is 1177.09 MTY and dust loss (2%) is 23.54 MTY, leaving 1153.55 MTY to be conveyed pneumatically to storage. The conveying air is exhausted to the atmosphere via cyclone and/or bag filter. The retained dust is returned to the process, but 9.60 MTY of the finest dust is lost.

Silicon feed is blended with a catalyst and stored under nitrogen, some of which bleeds off to a waste gas header. Bleed quantity is designed for 228.87 MTY.

Hydrogen gas conveys the prepared feed, together with recycle streams of silicon tetrachloride and hydrogen, to the hydrogenation reactor to produce trichlorosilane. The reacted stream proceeds to the waste settler, from which a waste stream is discharged to a liquid waste header. This waste stream amounts to approximately 1004 MTY and contains most of the impurities in the silicon feed (as metal chlorides) and most of the silicon loss. The breakdown is as follows:

$SiCl_4$	795 MTY
$SiHCl_3$	150 MTY
Heavy metal chlorides, as $CuCl_2$	52 MTY
Si	6 MTY.

The balance of about 1 MTY consists of hydrogen, nitrogen, HCl, SiH_3Cl, SiH_2Cl_2, and silane.

Product leaving the waste settler is cooled, the unreacted hydrogen is recycled, and crude trichlorosilane (TCS) is run to buffer storage. From there, it is transferred to a stripper to remove light ends. En route, it is passed through a filter, from which another waste stream is taken. This has the following composition:

Hydrogen	45 MTY
Dichlorosilane	34 MTY
Trichlorosilane	8.5 MTY

The remainder, 17.5 MTY, is about equally divided between nitrogen, HCl, silane, monochlorosilane, and silicon tetrachloride. This stream accounts for a discharge of 16 MTY of silicon and 38 MTY of chloride. It is discharged to a special waste gas header. There is a nitrogen bleed of indeterminate size from the crude buffer storage tank, and this also goes to the waste gas header.

The light ends are removed overhead from the stripper, condensed, and returned as reflux, except for a gaseous stream discharged to the waste gas header. The light end waste stream totals 75 MTY, of which nearly half is dichlorosilane (34.5 MTY), together with trichlorosilane (9 MTY), silane (8.5 MTY), monochlorosilane (3 MTY), hydrogen chloride (12.5 MTY), and the balance mostly hydrogen.

Subsequent processing of the triclorosilane stream by means of stills and "redistributing" reactors, generates a pure silane stream, which is then pyrolyzed to pure silicon, and a silicon tetrachloride stream, which is recycled to hydrogenation, via buffer storage.

The only other emission from the process comes from the silicon product melter, its composition being listed as approximately 0.3 MTY of hydrogen, 6 MTY of silane, and 425 MTY of argon. (The melting is performed under an argon atmosphere.)

Although Union Carbide's process description goes on to discuss waste disposal and the recovery of useful by-products,[7] this falls under control technology and is discussed in Section 7.0.

MANUFACTURE OF SINGLE-CRYSTAL SILICON CELLS FROM INGOT

For 1-MWp capacity of silicon photovoltaic cells manufactured by the ingot method, 12.87 MT of SeG-Si is required.[1] It is assumed that the material arrives at this stage of manufacture as a solid, which has to be crushed before melting. A 0.5% loss is sustained during crushing (0.06 MT/MWp), leaving a net of 12.81 MT/MWp to be melted.

According to one source,[3] after it is crushed, the silicon rod material must be cleaned with a mixture of trichloroethane, nitric acid, hydrofluoric acid, and water. However, the usage rate of the cleaning liquid is not stated, and since this step is not described elsewhere, it has not been considered.

The crushed silicon is melted in a crucible under an argon or helium atmosphere, and under slight vacuum. At this stage, the silicon is doped with boron, by introducing either chunks of silicon containing the required amount of the element (2.69 g/MWp) or a gaseous compound of boron such as boron trichloride or diborane (31.1 g/MWp of BCl_3 would be required). In the latter case, there is the possibility of forming HCl or boric acid as a pollutive by-product, but the quantities are minimal, and only the safety of factory personnel need be considered.

The crucible and ingot are rotated while a crystal is withdrawn at a controlled rate to form a cylindrical ingot. Of the original charge, 7% remains in the crucible as scrap, i.e., 0.9 MT/MWp.

To manufacture wafers from the ingot requires a series of mechanical steps, each resulting in the removal of silicon, as follows:

a)	Cropping tapered ends of ingot - 21% removed	2.50 MT/MWp
b)	Grinding ingot to required diameter - 3% removed	0.28 MT/MWp
c)	Sawing ingots into wafers - 45% removed	4.11 MT/MWp
	Total	6.89 MT/MWp

Most of the removed material is recoverable, either as recycle or as a marketable lower-purity material.

A slurry of equal parts by weight of oil, clay, and silicon carbide grit is used to saw the wafers. The circulation rate of the slurry is high, but about 1.07 MT/MWp is removed with the waste silicon. It would probably be washed away with water, in order to clean the silicon for recycle or sale, and have to be disposed of.

The sawed wafers must be treated to remove saw damage by immersion in a bath containing a mixture of nitric, hydrofluoric, and acetic acids. Acid consumption is as follows:

HNO_3	35.7 MT/MWp
HF	7.8 MT/MWp
CH_3COOH	12.5 MT/MWp

In the process, 1.91 MT/MWp of silicon is lost. Assuming it is discharged as SiF_4 (7.08 MT/MWp), the HF is reduced to 2.36 MT/MWp, and there is a hydrogen stream of 0.27 MT/MWp.

In the junction formation step, phosphorus is diffused into the wafer surface by exposing the wafers to phosphorus oxychloride vapor in a furnace. The theoretical requirement for phosphorus is 10.3 g/MWp, a miniscule amount. However, an excess of $POCl_3$ is used, which can potentially break down to HCl, P_2O_5, and Cl_2.

Next, the wafer edges are ground under water sprays. Only a small quantity of silicon dust is removed, 0.61 kg/MWp. Then, the wafers are etched to remove the SiO_2 layer formed during the diffusion process. The etchant is either hydrofluoric acid alone or in combination with nitric acid. In the former case 80.6 kg/MWp of HF is discharged, in the latter case 82.17 kg/MWp of HF and 35.8 kg/MWp of HNO_3. The process generates 1.42 MT/MWp of silicon tetrafluoride vapor, which must be disposed of. This quantity of SiF_4 implies the release of about 0.06 MT/MWp of hydrogen.

Metallization by electroless plating follows. Photoresist, a urethane varnish made thixotropic with titanium dioxide,[4] is applied to a batch of wafers by a squeegee over a stainless steel or plastic screen. Exposure to light fixes the resist. The wafers are then dipped sequentially into three baths. The first is a plating solution, essentially nickel hypophosphite with some ammonia and wetting agents, which requires ventilation. About 2.99 MT/MWp of solution is required and must then be disposed of. The second is acetone, to remove the photoresist. 2.14 MT/MWp of acetone is used to remove 740 liters/MWp of photoresist. If a recoverable solvent were used instead of the acetone, material consumption would be reduced. Last is a water rinse bath, whose water consumption is not stated.

The wafers are dried and sintered at 500°C under an atmosphere of nitrogen, then dipped in a flux bath (ventilated to remove chloride or formaldehyde fumes), followed by a solder bath (also ventilated). The wafers are finally washed with water, rinsed, and dried. Again, water consumption is not stated. For purposes of discussion, we can assume that 1.0 MT/MWp of water containing small amounts of acetone (or other solvent) and flux will require disposal.

Silicon nitride is deposited on the wafers as an antireflective coating. Chemical vapor deposition is the process employed, using dichlorosilane and ammonia as deposition gases. Nitride is deposited, and HCl and hydrogen are exhausted (3.2 and 0.18 kg/MWp, respectively). Some of the unreacted gases are also exhausted (1.7 kg/MWp of SiH_2Cl_2 and 0.11 kg/MWp of NH_3), and some Si_3N_4 is deposited on the walls of the reactor (0.45 kg/MWp).

Cells are subsequently tested, interconnected to form modules, encapsulated, and the modules tested. None of these processes can be considered to have significant emissions. In the interconnection step, fumes are given off in the solder reflow process, and in the autoclaving step of encapsulation, the ethylene vinyl acetate material used may give rise to some odor. These can be dealt with merely by adequate exhaust systems venting outside the factory building.

MANUFACTURE OF SINGLE-CRYSTAL SILICON CELLS FROM RIBBON

Semiconductor-grade silicon is melted and rises up by capillary action inside a graphite die. At the top of the die it solidifies in contact with a seed of silicon, which is then drawn upward at a rate such that molten silicon continues to cool in the die, and so generates a single-crystal ribbon. Emissions from this process are minimal. The solidified ribbon is scribed and cut into wafers, in which process a small amount of dust may be generated.

The cut wafers are delivered to a machine in which they are sprayed with a slurry of aluminum powder in ethanol, after which they pass through ovens where they are dried and fixed. During spraying, 0.383 MT/MWp of aluminum powder and 7.68 MT/MWp of ethanol are discharged. During drying, 3.29 MT/MWp of ethanol is vaporized. These operations are performed in a high-capacity air exhaust system, so that the emissions are considerably diluted.

The fixed wafers are transferred to a reaction chamber, in which a slight vacuum is applied, and an etchant gas is introduced to remove SiO_2. The gas is 8.5% oxygen and 91.5% carbon tetrafluoride, and radiofrequency energy is applied to generate active gas species. Reaction products are removed by a vacuum pump, and may include silicon tetrafluoride, silicon oxyfluorides ($SiOF_2$, Si_2OF_6), oxygen, fluorine, and carbon dioxide. Total quantities will be small.

Etched wafers are next conveyed to the ion implantation step. Phosphine gas, as a 15% mixture in hydrogen, is used as the phosphorus source, about 3.76 g (or 2.46 liters) of PH_3 being required per MWp. The process is performed under vacuum, and emission rates are estimated to be 1.88 g PH_3/MWp and 25.07 g/MWp of hydrogen. These gases are removed in a high-volume air exhaust system.

Wafers are sequentially metallized, first on the back, then on the front. A silver-based ink is applied by squeegee over a screen to print the pattern, and the wafers are then dried and sintered at 550°C. Excess ink is disposed of either when the screen is washed off with solvent, or when the screen itself is disposed of. A total of 1.793 MT/MWp of ink must be recycled or dumped, plus cleaning solvent. Further, although 0.237 MT/MWp of ink remains on the wafers, the vehicle fraction is evaporated during drying and must be vented.

Finally, the wafers are sprayed with an antireflective coating of titanium dioxide, carried in some liquid vehicle. The coated wafers are then dried and baked. It is estimated that 30% of the spray coats the wafers; the vehicle of this portion is evaporated during drying. The remaining 70% (125 liters/MWp) ends up on equipment and chamber walls, drying and losing its vehicle to the exhaust system. Solvent of some kind is then required to wash off the unwanted TiO_2.

The processes of cell testing, interconnection, encapsulation, and module testing are essentially emission free.

PRODUCTION OF CADMIUM SULFIDE-COATED SUBSTRATE

Cadmium metal is recovered from the wastes of zinc refining as a sponge of about 99.5% purity. An estimated amount of 0.606 MT of pure cadmium is required per megawatt capacity of CdS cells. The cadmium is purified to 99.995% purity by the process of "electrowinning," and is then reacted to form cadmium chloride. A solution of the latter, together with a solution of thiourea, is sprayed onto treated glass substrates. The mixture reacts to form cadmium sulfide as a solid deposit on the glass.

Four process steps are included:

Electrowinning--

Cadmium sponge is oxidized to CdO with steam, and the resulting material leached with spent electrolyte and sulfuric acid to generate new electrolyte, i.e., an aqueous solution of $CdSO_4$. The solution is filtered, and impurities are precipitated with a strong oxidizing agent, such as manganese dioxide. These impurities constitute the difference between 99.5% purity and 99.995%, i.e., approximately 0.5% or 0.00303 MT/MWp. They include some, or all, of the following arsenic, thallium, lead, iron, and copper, presumably as the oxides. The precipitate is filtered out, and the oxidizing agent will remain in solution as sulfate. Animal glue is added to enhance the smoothness of the cadmium cathodes obtained by electrolysis. The cathodes are removed every day, rinsed, and stripped. The stripped cadmium is melted and cast into shapes. The spent electrolyte is recycled to the leaching process, but, at some limiting concentration, a waste stream is bled off and disposed of.[4] If we assume that the MnO_2 is present in 100% excess, the solution to be disposed of [a mixture of MnO_2 and $Mn(SO_4)_2$] will contain about 0.00303 MT/MWp of Mn. This also presupposes that the effective average atomic weight of metals in the precipitate is about double that of manganese, allowing for differences in valence. The waste stream is also said[1] to contain 0.0079 MT/MWp of cadmium, presumably in the sulfate form.

Production of Cadmium Chloride--

$CdCl_2$ can be produced by direct reaction of the metal with chlorine gas or HCl gas. It can also be produced in solution by reacting the metal with aqueous HCl. Since it is required as a solution in the CdS deposition step, the latter method would appear to be more appropriate. The literature does not identify the specific process employed. There should be no difficulty in attaining a reasonable solution concentration, because the solubility of

$CdCl_2$ in water at 20°C is 140 $CdCl_2$/100 g water.[6] The required amount of $CdCl_2$ is 1.00 MT/MWp. With pure reactants, the only emission to be expected is hydrogen, at the rate of 0.01 MT/MWp.

Processing of Glass Substrates--

Precut glass wafers are washed and air dried, then heated in a radiant oven and sprayed with a solution of tin chloride[1] in methanol. In contact with the hot glass, the tin chloride and methanol react to form tin oxide,[1] which is deposited in a film 0.5 μ thick.[4] Emissions are stated[1] to include a tin chloride of unknown form, tin oxide, and formic acid. The process is not quantified, but the "major emission" is said to be tin chloride, "a hydroscopic white powder." $SnCl_2$, anhydrous or hydrated, is a white powder, as are various hydrates of $SnCl_4$. Anhydrous $SnCl_2$ would appear to be a likely candidate. The required thickness of tin oxide is equivalent to 0.072 MT/MWp as SnO_2. The reaction between $SnCl_2$ and methanol requires additional oxygen from the air, and results in the generation of one mole of formic acid and two moles of HCl for every mole of SnO_2.[5] Thus, emissions include 0.022 MT/MWp of formic acid and 0.035 MT/MWp of HCl. Furthermore, assuming a spray efficiency of 30%, a commonly cited figure for similar processes,[1] 0.179 MT/MWp of $SnCl_2$ is lost. The stoichiometry of the SnO_2 reaction requires equimola quantities of $SnCl_2$ and methanol. However, the actual mixture used probably has a substantial excess of methanol, in order to keep the $SnCl_2$ in solution, or in suspension. The equimolal quantity of methanol would be 0.030 MT/MWp. We assume a lost rate, however, of 0.5 MT/MWp.

Cadmium Sulfide Application--

This step is similar to the previous step, except that the spraying mixture consists of (aqueous) solutions of $CdCl_2$ and thiourea. In contact with the heated substrate, these react to deposit a layer of CdS. The quantity of $CdCl_2$ needed to deposit the required thickness of CdS is 0.50 MT/MWp. The spray efficiency is expected to be 50%,[1] which means that the same quantity of $CdCl_2$ is lost (or the equivalent in sulfide and other compounds). Similarly, 0.203 MT/MWp of thiourea is lost, because of spray inefficiency, plus 0.118 MT/MWp of breakdown products of reacted thiourea. The latter could include ammonia and hydrogen cyanide.

MANUFACTURE OF BACKWALL CdS CELLS

The first step in the next sequence of operations is to remove the CdS coating in a grid pattern, so that a grid of metallized lines can be subsequently applied. This is done mechanically by scraping off the CdS, down to the SnO layer, using a needle-shaped instrument. The exposed SnO is then vaporized away by a laser beam.

CdS dust is removed by a vacuum cleaner, at the rate of about 2 kg/MWp and is then placed in containers for recovery or landfill. About 0.6 kg of SnO will be vaporized per MWp. After exposing the glass substrate, two layers of resist are laid down by pens. Only limited quantities of waste are produced.

In the next step, two copper ions replace each cadmium ion in the surface of the CdS layer. This is completed by passing the cells through a series of tanks containing a proprietary copper chloride solution.[1] Elsewhere the solution is identified as saturated.[4] Presumably, the solution contains other solutes beside CuCl, but these are not known. A saturated solution of CuCl in cold water contains 62 mg/l.[6]

The amount of copper required is estimated to be 0.089 MT/MWp, displacing 0.0787 MT/MWp of cadmium. The ion exchange process is said to be 50% efficient in copper, so that the fresh solution contains 0.178 MT/MWp of copper, or 0.277 MT/MWp of CuCl. In saturated solution, this would require 4.473 m^3 of water. The concentration of CuCl in the spent solution will be half the original, i.e., 31 mg/l, and there will also be 29 mg/l of $CdCl_2$. These concentrations are equivalent to 20 mg/l of Cu and 18 mg/l of Cd.

After the ion exchange step, the cells are rinsed in deionized water. Metallization is carried out in a vacuum chamber, and pellets of three metals are evaporated in sequence, 35% depositing on the cells, the rest depositing on the vacuum chamber walls and fittings, or being exhausted through the vacuum system. Copper is laid down to a thickness of 0.7 μ, followed by a 2.0-μ thickness of lead. The third metal is proprietary, but elsewhere, Inconels and aluminum are mentioned. The quantities of copper and lead not deposited on the cells are 0.207 and 0.753 MT/MWp, respectively.

Subsequent assembly steps include; attaching electrical connections, encapsulation, test and frame assembly. Emissions from these processes are minimal, e.g., solder fumes and plastics odor. Ventilation is required.

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